THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

# HYDROUS SLUDGES. RELATIONSHIP BETWEEN THE CONSTITUTION AND DEWATERING PROPERTIES

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# HYDROUS SLUDGES. RELATIONSHIP BETWEEN THE CONSTITUTION AND DEWATERING PROPERTIES

## SUMMARY


### OBJECTIVE

The objective of the program was to develop an understanding of the relationship between the constitution and the dewatering properties of hydrous sludges from pulp and paper mill clarification systems, with particular emphasis on those aspects of the relationship which are relevant to engineering studies of mill dewatering systems.

### OBSERVATIONS

A preliminary characterization of four representative sludges indicated that better than 90 to 95% of the solids were derived from pulps. A large portion of the solids were fines (through 200 mesh). Difficulty of separation was found to be associated with a high groundwood fines levels and a relatively high content of swellable polysaccharides.

A more detailed characterization of two sludge samples and a groundwood pulp from one of the mills confirmed the importance of the fines fraction. It also indicated that the fines have a higher relative content of the swellable hemicelluloses and pectin than the other fractions or the whole samples.

Studies of sedimentation behavior indicated that both size effects and chemical composition influence separation in the free-fall phase where each particle is away from the influence of other particles. They also revealed that, for sludge solids, interparticle contact begins in the

consistency range of 3 to 4%. Thus, further separation is dominated by the compressibility and drainage characteristics of the compacted solid mass rather than by the density differential usually considered the dominant factor in centrifugation.

Investigation of the higher consistency regions, which more closely approach the consistencies desired in practice, was based on the centrifugal water-retention method. In this technique, pads formed from a dispersion can be subjected to a centrifugal field in a configuration which permits drainage of interstitial water. The drainage time measured during formation of the pad provides a measure of the filterability of the dispersion while the final solids content after centrifugation indicates the capacity of the solids to bind water. The influence of both particle size and hemicellulose content were explored by this method.

Final solids content was found to vary with particle size but not very significantly with hemicellulose content. The drainage time, which is more closely related to dewaterability in practical systems, varied quite significantly with hemicellulose content on the other hand. Thus, it was established that removal of swellable polysaccharides can bring about substantial enhancement of dewatering rates.

The effects of treatments which remove the polysaccharides were explored further in isotope exchange studies and in the Scanning Electron Microscope. Both studies suggested an increase of fibrillation as the content of swellable polysaccharides was reduced.

An exploratory study was also carried out in which amine-modified clays were added to fiber dispersions and the effect on drainage time measured.

The result was a reduction in drainage time. The Scanning Electron Microscope revealed that the modified clay particles seem to interact with the fibrils in such a way as to minimize their capacity to clog up the interstices. Thus, the porosity of the compacted solids is increased.

## CONCLUSIONS

The primary conclusion is that practical dewatering problems must be understood in terms of rate-determining phenomena rather than equilibrium limitations. The major portion of the water to be removed in attaining a solids content of 30 to 40% does not differ in any thermodynamic sense from free water. Thus, the problem is one of configuration at a macroscopic level rather than of association at a molecular level.

The problems associated with separation of the water arise from a coupling of hydrodynamic effects with the mechanical properties of the suspended particles. The significant mechanical properties include the dimensions and the deformation characteristics. The latter are in turn determined by chemical composition and degree of swelling.

Separation rates in the low-consistency region (<4%) are determined by free-fall phenomena parameters which include surface-to-volume ratio, the density differential between the particles and water, and the intensity of the potential field (g).

At 4 to 5% solids content, interparticle contact is established and drainage phenomena determine separation rates beyond this consistency range. The influence of the different sludge variables on drainage rates can be rationalized in terms of their influence on porosity. In particular, the effects of particle size and of composition can be understood on this basis.

Treatments which are known to improve dewaterability, such as heat treatment, freezing, or addition of particulates, can be understood in terms of their effect on porosity.

FUTURE DIRECTIONS

It is suggested that a program be undertaken to develop guidelines which will help mill personnel in choosing the sludge treatment methods most compatible with available disposal options. Particular attention is given to the possibility of recycling.

INTRODUCTION

The hydration characteristics of sludges from clarifiers in pulp and paper mills pose difficult engineering design problems. The complex nature of the interaction of water with the dispersed organic particles makes prediction of dewatering behavior a hazardous task. Thus, the design of dewatering systems proceeds, in most instances, by the very costly trial and error approach.

In order to reduce the element of risk in the design of dewatering systems, the NCASI has at different times sponsored and undertaken investigations of the properties and behavior of clarifier sludges (1, 2). It has also compiled a 'Manual of Practice for Sludge Handling in the Pulp and Paper Industry' (3), which in addition to summarizing the then current understanding of the properties of sludges, describes exploratory investigations of new approaches to dewatering. More recently, the council has sponsored efforts to understand the basic physical processes which might influence the behavior of pulp and paper mill sludges (4, 5). The work to be reported below represents an effort to understand some of the <u>chemical</u> factors which determine sludge behavior, and to relate these factors to other variables which combine to control the overall response of the sludges to dewatering systems. As set forth in the proposal (6) the objective was: "To develop an understanding of molecular level phenomena which dominate in hydrous sludges formed during the treatment of pulp and paper mill effluents, with emphasis on factors which determine the dewatering characteristics of these sludges." Since other NCASI programs currently in progress are concerned with dewatering methods, the exploration of new dewatering techniques was specifically excluded from the present program (7).

Receiving particular emphasis during much of the work were sludges which present the greatest difficulty in dewatering. These are the sludges from primary clarifiers of mills utilizing predominantly groundwood pulps, from the primary clarifiers of waste-paperboard mills, and from many different secondary clarifiers (7). The great difficulty encountered in dewatering such sludges has caused them to be regarded as stable gels, and to be labelled "hydrogels" (1). In what follows, these sludges will be referred to as "hydrous sludges" in order to avoid confusion concerning the state of aggregation at the molecular level.

In the proposal, it was noted that the sludges listed above as particularly difficult to dewater are likely to contain an excessive amount of water-swellable polysaccharides. It was hypothesized that the presence of such polysaccharides is, at least in part, responsible for the difficulty in dewatering. The basis of the hypothesis was that groundwoods are not subjected to the severe extractive conditions which occur in chemical pulping processes, and they are therefore likely to retain a substantial fraction of their water-swellable hemicelluloses and pectic substances. In the case of the secondary sludges it was anticipated that the capsular polysaccharides of the microorganisms, the natural function of which is prevention of rapid dehydration of the organism, would act to slow down dewatering of the sludges. The question of the validity of the hypothesis concerning the role of the polysaccharides motivated some aspects of each phase of the present investigation.

At the suggestion of Dr. I. Gellman, of the Council, the effort during most of the period of the work was focussed on the sludges from primary clarifiers of mills utilizing groundwood. This was in part in order to avoid dilution of the effort, and in part in recognition that the problems associated with biological sludges are receiving considerable attention from nonindustry sources.

The investigation was undertaken in a number of phases. The first was concerned with establishing the constitution of the sludges and defining the relevant constitutional variables. Representative sludges were obtained from cooperating mills designated by Dr. I. Gellman (8), and subjected to both chemical and mechanical characterization procedures. The findings are outlined in the next section on Characterization.

The results outlined in the Characterization section provided a basis for posing some questions concerning the relationship between the constitutional variables and dewatering behavior. In order to answer these questions it was necessary first to establish the ranges of the constitutional variables in typical sludges. The results for two representative sludges and a pulp derived model system are outlined in the section on Constitutional Variables.

The first group of dewatering phenomena investigated were those prevailing in the low-consistency region (below 4%) where the rates are dominated by single particle properties. Thus, the relationship of the constitutional variables to the parameters of separation in a potential field, whether centrifugal or gravitational, were explored. The results of this phase are summarized in the section on Separation at Low Consistencies.

In the next phase, attention was focussed on separation of solids in the region of most practical difficulty, that is the region between 5 and 25%. A substantial amount of water must be removed in accomplishing this transition, and the rates of separation are dominated by complex phenomena which are brought into play by the contact between particles. This contact results in formation of a solid mass with a porous structure which is extremely sensitive to the constitutional variables of the parent sludge. The influence of these variables was explored in an investigation of their effect on the Centrifugal Water Retention (CWR) capacities of suitably formed pads. These investigations are described in the section on Separation at High Consistencies, which is somewhat more detailed because much of this work has not been reported previously.

In an effort to develop further insight into the phenomena prevailing at the higher solids levels, some additional investigations were carried out on samples prepared during the Centrifugal Water Retention studies. These included isotope exchange measurements to establish the accessibility to hydration of some of the samples, Scanning Electron Microscopic (SEM) examination of many of the samples, and exploration of the influence of chemically modified clays on the compaction patterns of the solids to be dewatered. All of these additional investigations are described in the section on Other Studies.

The Discussion section is concerned with an overview and an interpretation of the results outlined in the preceding sections, and their relationship to prior knowledge of the systems of interest. Further, it is concerned with elaborating the emerging picture of different dewatering regimes dominating at different consistency levels and responding differently to variations in the constitutional variables of the sludges.

In the section on Dewatering Mechanisms the picture which has been developed is used as the basis for some thoughts on the mechanisms of dewatering in practical operating systems, and on treatments which are known to enhance dewatering rates.

The section on Future Directions is concerned with discerning the most promising directions for future efforts.

## CHARACTERIZATION

The group of sludges chosen for initial investigation were from the primary clarifiers of four mills designated by Dr. I. Gellman as providing representative samples. The mills supplying the sludges were: Southland Paper Mills, Inc., Lufkin, Texas; International Paper Company, Mobile, Alabama; Bowaters Southern Paper Corporation, Calhoun, Tennessee; and Kimberly-Clark Corporation, Coosa Pines, Alabama. The sludges from these mills have been labelled sludges A, B, C, and D, respectively, and this designation will be used in the following discussion. Sludges from the Lufkin mill received special emphasis throughout the work because it was identified by Dr. Gellman as experiencing the greatest difficulty in dewatering operations.

The characterization of the sludges involved both mechanical and chemical methods. These included microscopic examination, classification on the Bauer-McNett fiber classifier, and chemical analyses for a variety of wood pulp constituents. In addition, the sedimentation behavior of the sludges was explored in search of preliminary correlations between constitution and dewaterability. The results are summarized in what follows. A more detailed discussion was given elsewhere (9).

### MICROSCOPIC EXAMINATION

Microscopic examination of the sludges revealed that, in all cases, at least 90% of the solids were wood pulp fibers and fines. In both Samples A and D, pulp-derived components were in fact in excess of 95% of the total solids. The groundwood content of three of the sludges was quite high, ranging from 71% in Sludge D to 95% in Sludge A. The fourth sludge, B, had a groundwood content of only 14%.

Distinguishing features of Sludge A were that it had the highest groundwood content and that it was the only sludge in which the pulp-derived components were entirely of southern yellow pine. Sludges C and D were mostly of southern yellow pine, but both contained small amounts of hardwoods. Sludge B had a hardwood content of 39%.

CLASSIFICATION

Classification using a Bauer-McNett fiber classifier was undertaken to establish the particle-size distributions for the sludges. Slurries from each sludge were put through the classifier twice, once using 14-, 20-, 35-, and 60-mesh screens, and once using 60-, 100-, 150-, and 200-mesh screens. The major finding was that, for all four sludges, the fraction passing through the 200-mesh screen was at least twice the amount expected for a typical groundwood.

CHEMICAL ANALYSES

The chemical analyses were intended to establish the types of polysaccharides present and initially consisted of sugar analyses. It was found that the distributions of sugars were consistent with the findings of the microscopic examination concerning the wood species present in each of the sludges. Another important finding was the presence of significant quantities of galacturonic anhydride, indicating that pectic substances do indeed occur in large enough quantities to influence the hydration of the sludges. Furthermore, Sludge A had a higher level of pectic substances than the others.

SEDIMENTATION

The sedimentations were carried out both in the gravitational field and in a laboratory centrifuge. For the gravitational sedimentation, an initial consistency of 0.3% was used in a 500-ml. graduated cylinder. The results, which are shown in Fig. 1, indicate that Sludge A is the slowest to separate.

The centrifugal sedimentations were initially carried out at a number of speeds. It was found that a rotational speed of 500 r.p.m.[1] gave the best resolution of the behavior of the sludges, and it was therefore adopted as the basis for further comparisons. In order that the results for the different sludges be comparable, the sedimentations were carried out at the consistency of Sludge A which had the lowest initial consistency (1.4%). The sedimentation curves are shown in Fig. 2. Here again it was found that Sludge A separated least under the influence of the potential field.

In addition to the sedimentation studies on the sludges, sedimentation rates were measured for a sample of Canadian spruce groundwood which was immediately available. Its behavior in both gravitational and centrifugal sedimentation was similar enough to those of the sludges to suggest the possibility of using groundwood pulps as model systems.

[1]The relative centrifugal force (g) at the tip of the centrifuge is 55 at a rotational speed of 500 r.p.m. It must be kept in mind that, because the centrifuge tube is of finite height, g is not constant throughout.

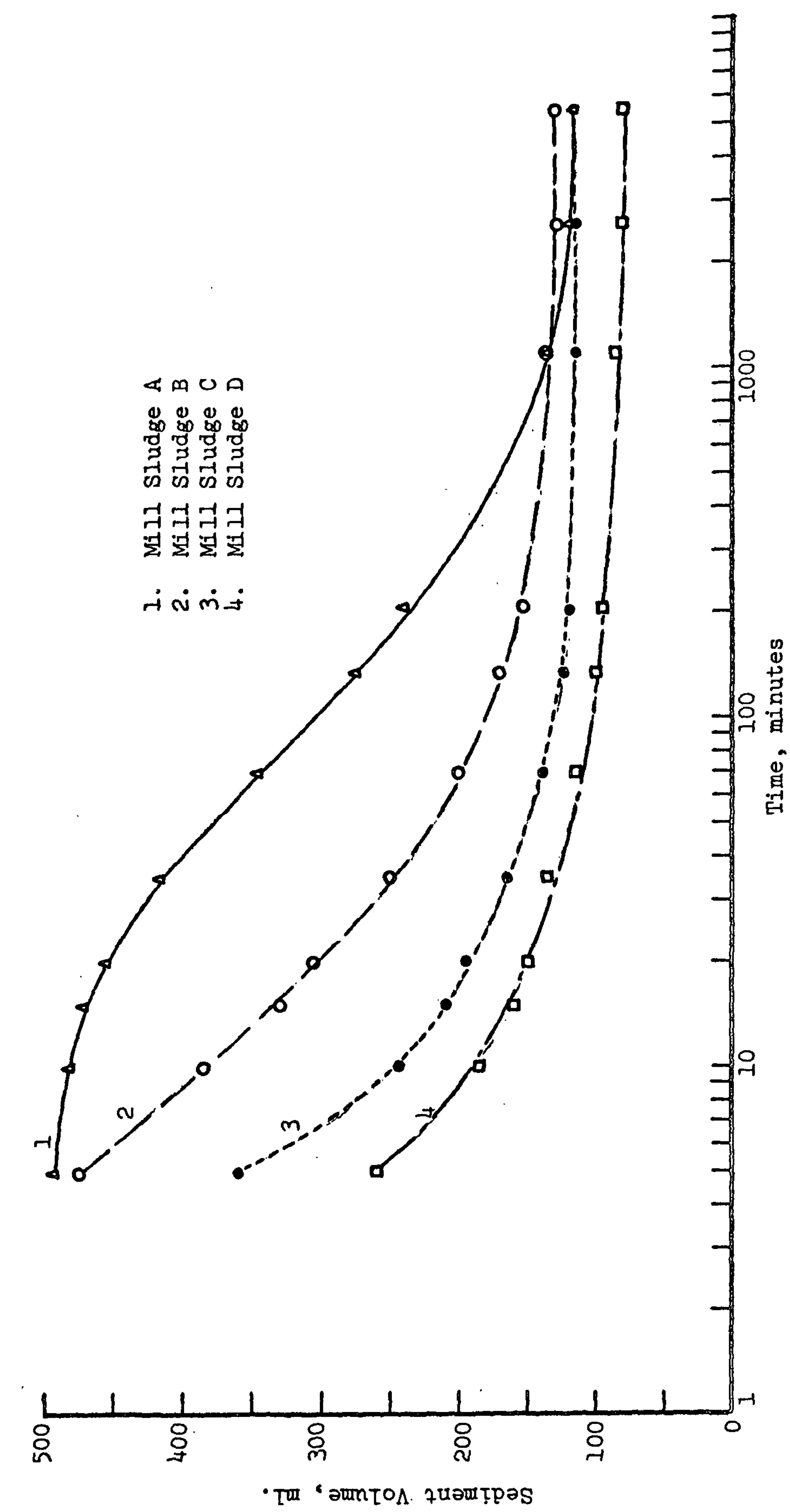



Figure 1. Comparative Settling Tests of Diluted Sludges (500 ml. at 0.3% Consistency)

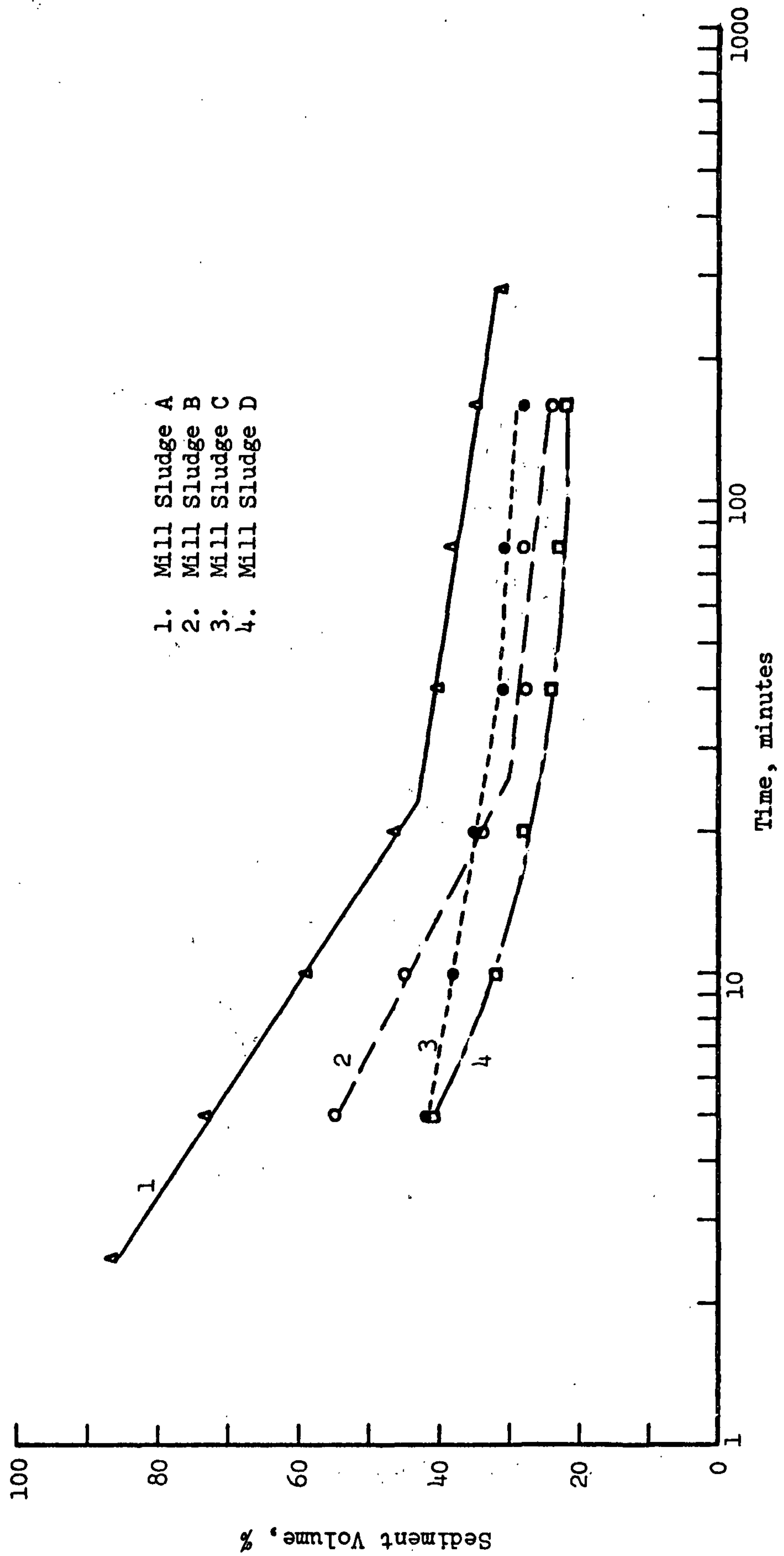



Figure 2. Sediment Rates of 4 Sludges (1.4% Consistency, 500 r.p.m.)

## FURTHER CHARACTERIZATIONS

During the later phases of the program, additional samples of primary sludges were secured and characterized. Two samples from the Lufkin mill, designated Sludges A-2 and A-3, were subjected to characterization procedures similar to those outlined above for the first group of sludges. The results will be discussed in the following sections.

## PRELIMINARY CONCLUSIONS

The most important preliminary conclusion was that the sludges are closely related to the pulps in use at the source mills. This then provided a basis for developing model systems from the pulps or fractions of the pulps. It also suggested the choice of constitutional variables which have been used in the past for the characterization of pulps.

It was clear from the preliminary characterization that the high fraction of fines (through 200-mesh) must be a factor in the poor dewaterability of the sludges, for all the sludges had a very high fines fraction. Thus, the particle size distribution was chosen as one of the important constitutional variables.

The finding that Sludge A had a higher relative content of pectic substances suggested that, while particle size distribution may be a major factor in dewatering behavior, the content of swellable polysaccharides must also be an important factor, for although Sludge D had a larger fraction of fines than Sludge A it separated more easily in sedimentation studies. Thus, the contents of swellable hemicelluloses and pectin were chosen as the second major constitutional variable.

It should be noted that the definition of the constitutional variables has the primary sludges in mind. Modifications of definitions would be necessary in attempts to interpret the behavior of other sludges.

## BIOLOGICAL SLUDGES

In order to explore the relevance of the investigations of primary sludges to the behavior of biological sludges, a group of three biological sludges were subjected to preliminary chemical analyses focussing primarily on the sugar content. The samples were obtained from the Downington Paper Co., Division of Sonoco Products Co., in Downington, Pennsylvania. They included samples of a secondary sludge before and after chlorine treatment, as well as a sample of a mixed secondary and primary sludge. The results of the sugar analyses are given in Table I. The outstanding feature is the very high content of rhamnam in the two secondary sludges. This is a distinguishing feature of a number of bacterial capsular polysaccharides (10), and provide direct evidence for the presence of substantial quantities of these polysaccharides in the secondary sludges. The higher glucan, xylan, and mannan contents of the combined sludge are consistent with a high fiber content.

TABLE I

SUGAR ANALYSIS OF BIOLOGICAL SLUDGES

| Sample | Rhamnan, % | Araban, % | Xylan, % | Mannan, % | Galactan, % | Glucan, % |
|---|---|---|---|---|---|---|
| Waste activated sludge before chlorine treatment | 1.3 | 0.2 | 0.2 | 1.2 | 1.5 | 5.3 |
| Waste activated sludge after chlorine treatment | 1.3 | 0.2 | 0.9 | 1.2 | 1.2 | 8.8 |
| Combined primary underflow and waste activated sludge | 0.4 | 0.6 | 6.0 | 5.1 | 1.1 | 43.6 |

All values represent single determinations.

Basis: Moisture free (dried under vacuum over $P_2O_5$).

## CONSTITUTIONAL VARIABLES

The results of the characterization of the first four sludges led to formulation of questions concerning the relationship between the constitutional variables and the behavior of sludges in dewatering systems. The first of these questions arises from the observation that a substantial fraction of each of the sludges is smaller than 200-mesh. Indeed the size of this fraction seems, at first, the only difference between the sludges and a typical groundwood. It must therefore be established whether the properties of this fraction dominate the behavior of the sludges. A logical search for an answer to this question would include a size fractionation followed by investigation of the dewatering behavior of the different fractions.

Another question which arose, perhaps less directly, was whether the pattern of mechanical fragmentation accomplished by the grinding process is accompanied by a chemical differentiation. If this were the case, and if the fines were richer in the hemicelluloses, then the effect of the large fines fraction could be magnified. It seemed worthwhile, therefore, to explore the variation of chemical composition with particle size.

A third question concerned the development of a meaningful model system. The results of the characterizations reported in the previous section had revealed a closer relationship between the sludges and the pulps in use at the source mills than had been anticipated. It seemed desirable, therefore, to explore the parallels between the sludges and the pulps.

In order to develop some answers to the questions posed, and in order to establish the ranges of the constitutional variables, the decision was taken to focus on the sludges and the pulp from the Lufkin mill. The second sample of sludge was obtained from the mill together with a sample of the groundwood pulp in use at the mill. These samples were designated Sludge A-2 and groundwood SP, respectively, the designation of the latter reflecting the finding that it consisted, almost exclusively, of southern yellow pine. At a point later in the program it was thought desirable to establish the reproducibility of the findings on Sludge A-2. A third sample of sludge was obtained from the Lufkin mill, designated Sludge A-3, and subjected to the same types of investigations as Sludge A-2. Sludges A-2 and A-3 were received 19 weeks apart in time.[2]

## FRACTIONATION

The first step taken to define the range of the constitutional variables involved a fractionation of the samples in a manner similar to that outlined above for the first group of sludges. The results for the two sludges and the groundwood are compared in Fig. 3. It is clear from the comparison that the two sludges are quite similar in particle size distribution, so that, at least with regard to this aspect of their character, Sludge A-3 reproduces Sludge A-2 quite well. In the comparison to the groundwood pulp, the outstanding feature, again, is the much lower content of the "through 200-mesh" fraction in the pulp, and the higher content of all the larger fractions, except shives (on 14-mesh).

[2]It should be noted that no effort was made to compare Sludges A-2 and A-3 with Sludge A for the following reason. The Lufkin mill has two primary clarifiers, one of which receives the sludge from secondary clarifiers in addition to the primary effluent stream. Sludge A was erroneously supplied from the clarifier receiving the secondary sludge, while Sludges A-2 and A-3 were taken from the clarifier receiving only the primary effluent stream.

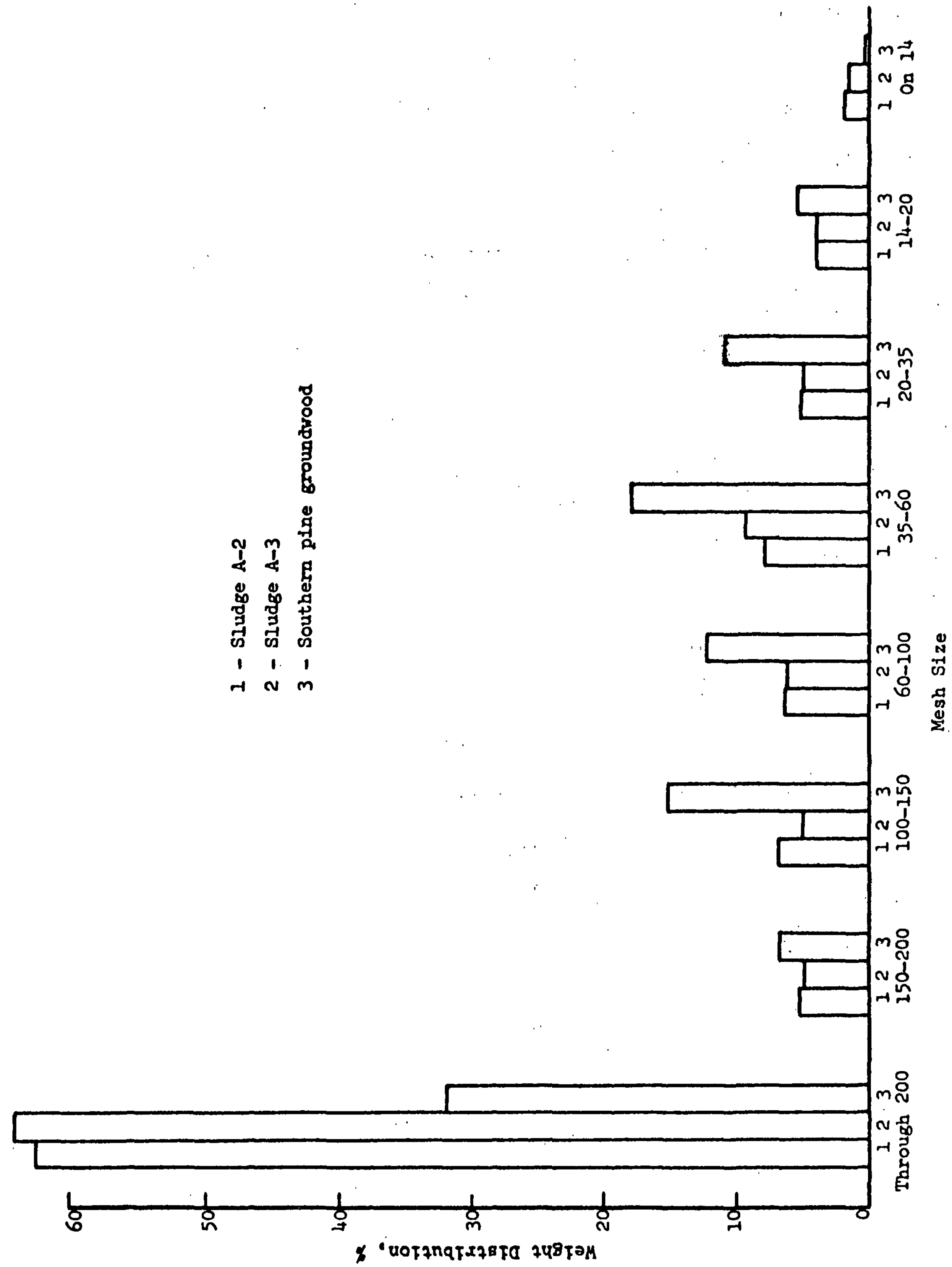



Figure 3 Bauer-McNett Classification of 2 Sludges and Groundwood Pulp

While the separation into eight fractions obtained in the double classification is essential to developing a view of the particle size distribution, it did not seem economically feasible to subject all the fractions to the types of investigations contemplated. A coarser fractionation was therefore carried out to provide samples in large enough quantities for these studies. This consisted of a classification resulting in three large fractions. The first, designated "on 60," includes all particles retained on a 60-mesh screen. The second, designated "through 60," includes all particles passing through a 60-mesh screen. The third fraction, designated "through 200," includes all particles passing through a 200-mesh screen, and is the only one having a corresponding fraction in the finer fractionation reported above. The investigations, in most instances, were carried out for the three large fractions as well as for the unfractionated sample designated "whole."

## CHEMICAL ANALYSES

The three fractions and the "whole" samples of Sludges A-2 and A-3 and of the groundwood pulp were subjected to analyses which were more comprehensive than those carried out for the first group of sludges in that they included analyses for wood components other than sugars. Although the results have been reported previously (11) they have been reproduced in Tables II, III, and IV for convenience of reference.

A number of important observations emerge from the chemical analyses. The first is the clear indication of significant variation of composition with particle size. The magnitude of the variation is greater for the sludges than for the groundwood SP, though even in the latter the differences are quite significant.

TABLE II

CHEMICAL ANALYSIS — SLUDGE A-2

| | Whole, % | On 60, % | Through 60, % | Through 200, % |
|---|---|---|---|---|
| Araban | 1.1 | 1.0 | 1.3 | 1.3 |
| Xylan | 5.2 | 7.05 | 5.8 | 5.6 |
| Mannan | 7.9 | 10.65 | 8.4 | 8.0 |
| Galactan | 2.7 | 1.85 | 2.8 | 3.4 |
| Glucan | 34.5 | 52.4 | 35.9 | 32.1 |
| Galacturonic anhydride[a] | 0.47 | 0.405 | 0.54 | 0.65 |
| Lignin | 25.1 | 18.8 | 27.4 | 29.3 |
| Nitrogen | 0.16 | 0.055 | 0.155 | 0.15 |
| Extractives (alcohol-benzene) | 11.0 | 3.81 | 8.52 | 9.85 |
| Ash | 2.94 | 1.10 | 2.96 | 2.73 |

[a]Pectin contains approximately 80% galacturonic anhydride.

Results are based on moisture-free fractions.
Analyses include components of interest to the study. Totals are less than 100%.

TABLE III

CHEMICAL ANALYSIS — SLUDGE A-3

| | Whole, % | On 60, % | Through 60, % | Through 200, % |
|---|---|---|---|---|
| Araban | 1.0 | 1.0 | 1.1 | 1.1 |
| Xylan | 5.3 | 7.2 | 5.1 | 4.8 |
| Mannan | 7.6 | 11.0 | 7.2 | 6.6 |
| Galactan | 2.4 | 1.9 | 2.8 | 2.7 |
| Glucan | 33.1 | 49.9 | 31.7 | 28.3 |
| Galacturonic anhydride[a] | 0.34 | 0.10 | 0.23 | 0.29 |
| Lignin | 24.0 | 19.8 | 25.5 | 26.0 |
| Nitrogen | 0.20 | 0.04 | 0.25 | 0.32 |
| Extractives (alcohol-benzene) | 12.1 | 1.3 | 11.8 | 14.2 |
| Ash | 5.2 | 1.6 | 5.4 | 6.0 |

[a]Pectin contains approximately 80% galacturonic anhydride.

Results are based on moisture-free fractions.
Analyses include components of interest to the study. Totals are less than 100%.

TABLE IV

CHEMICAL ANALYSIS — SOUTHERN PINE GROUNDWOOD

| | Whole, % | On 60, % | Through 60, % | Through 200, % |
|---|---|---|---|---|
| Araban | 1.3 | 1.1 | 0.8 | 1.3 |
| Xylan | 6.7 | 6.5 | 6.2 | 5.7 |
| Mannan | 11.3 | 12.4 | 10.4 | 9.0 |
| Galactan | 3.3 | 2.0 | 3.3 | 3.5 |
| Glucan | 40.9 | 43.1 | 38.9 | 34.7 |
| Galacturonic anhydride[a] | 0.36 | 0.26 | 0.36 | 0.43 |
| Lignin[b] | 27.56 | 25.55 | 28.68 | 32.18 |
| Nitrogen | 0.06 | 0.03 | 0.08 | 0.07 |
| Extractives (alcohol-benzene) | 4.18 | 0.86 | 2.63 | 2.42 |
| Ash | 0.77 | 0.66 | 1.26 | 1.76 |

[a]Pectin contains approximately 80% galacturonic anhydride.

[b]Not corrected for ash.

Results are based on moisture-free fractions.
Analyses include components of interest to the study. Totals are less than 100%.

The nature of the variation in chemical composition is also quite relevant. The lower glucan content in the smaller particles suggests a higher content of hemicelluloses relative to cellulose. Although the lignin content is higher in the smaller particles, the net effect remains a significantly higher proportion of hemicelluloses in the smaller particles.

The relevance of the increase in hemicellulose content is enlarged when one examines the nature of the change in greater detail. As discussed at length elsewhere (11), analyses of the ratios of the different sugar components reveals that the hemicelluloses which occur in larger quantities in the smaller particles are hemicelluloses which, in the absence of lignin, are more soluble in water, and which therefore, in the presence of lignin, are more readily swollen.

Another constituent closely related to the hemicelluloses is pectin. Although it occurs in smaller quantities than the hemicelluloses, it is important because of its capacity to bind large quantities of water. The content of pectin, reported as galacturonic anhydride, is also found to be higher in the smaller particles.

Another important observation revealed in comparison of the tabulated analytical data is the degree to which the compositions and the distributions of components are similar in the two sludge samples. Comparison of the sludges with the groundwood is also interesting. It reveals that the composition of the "whole" groundwood sample is intermediate between the "on 60" and "through 60" samples. In the case of the sludges, however, the "whole" sample is closer to the composition of the two smaller fractions. This is consistent with the particle size distributions and suggests that when the differences between the distributions are accounted for, the pulp can be taken as approximating the sludges quite closely.

## SEPARATION AT LOW CONSISTENCIES

It was clear from the first group of sedimentation studies that the separations necessary for dewatering occur in two different consistency ranges, and that in each range the rates of separation are determined by a different set of parameters. This is illustrated in Fig. 2 where the data for Sludge A show the sharpest break between the two ranges. In order to clarify the relationship between the constitutional variables and the behavior of the sludges in sedimentation a series of experiments were carried out on the fractions of Sludge A-2 and groundwood SP. The results have been reported in greater detail elsewhere (11), but, again, will be summarized here for ease of reference.

The sedimentation curves for the different fractions of Sludge A-2 and groundwood SP are given in Fig. 4 and 5. Two features stand out in a comparison of the sedimentation curves. The first is the great similarity between the curves for the different fractions of the sludge and those of the corresponding fractions of the groundwood. The largest difference occurs between the curves for the whole samples, and this is to be expected. These observations lend additional support to the assumption that the groundwood pulp provides a suitable model system.

The second feature which is worthy of note is the degree to which the curves for the different fractions are resolved. Clearly, the response of the dispersions to a potential field is strongly influenced by particle size.

The question of the dominance of a particular fraction in determining the behavior of the whole is a more complicated one. It is clear from Fig. 4 and 5 that the behavior of the "whole" samples, at least in the early part of

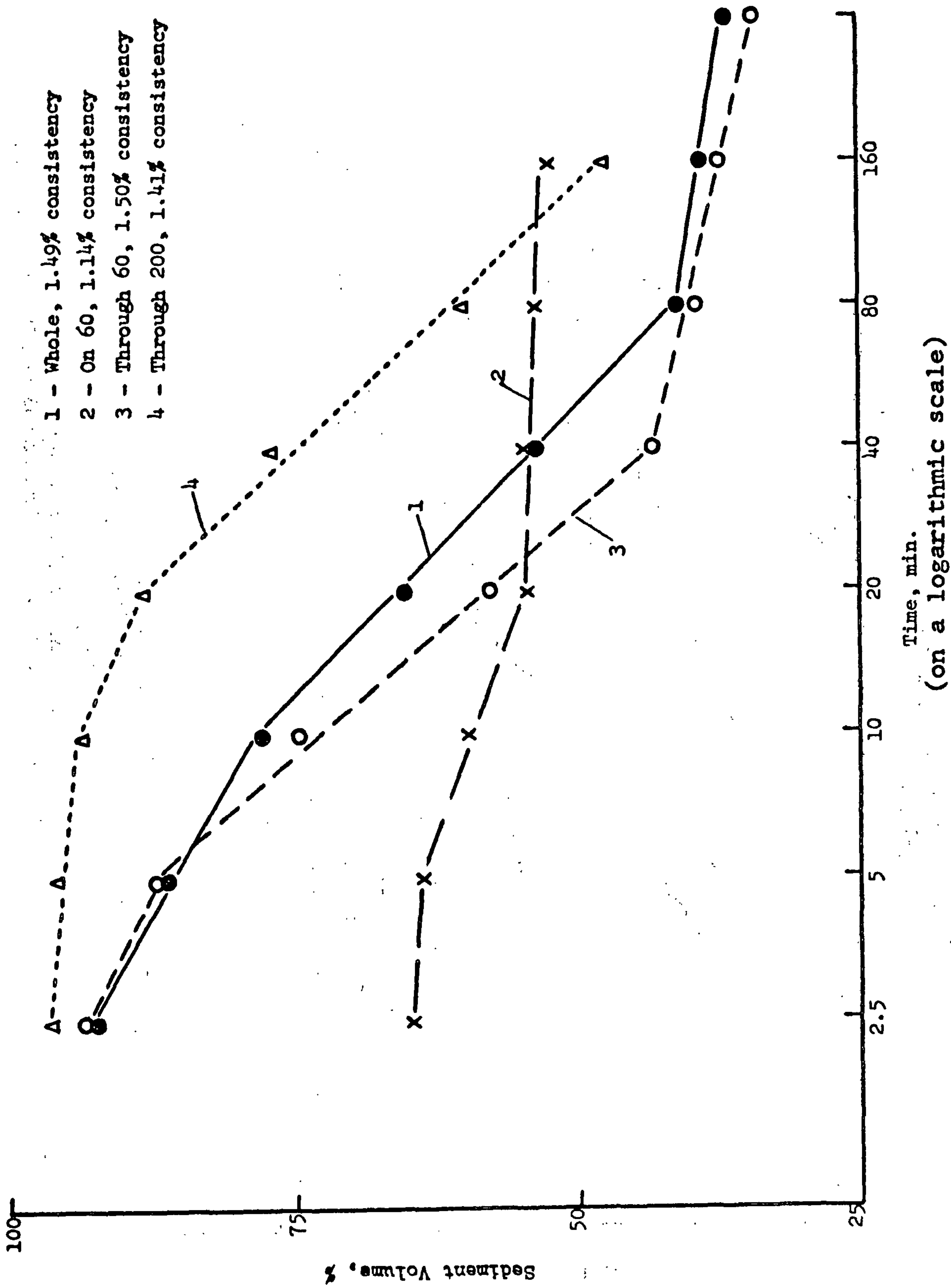



Figure 4 Centrifugal Sedimentation, Sludge A-2 and Fractions, 500 r.p.m.

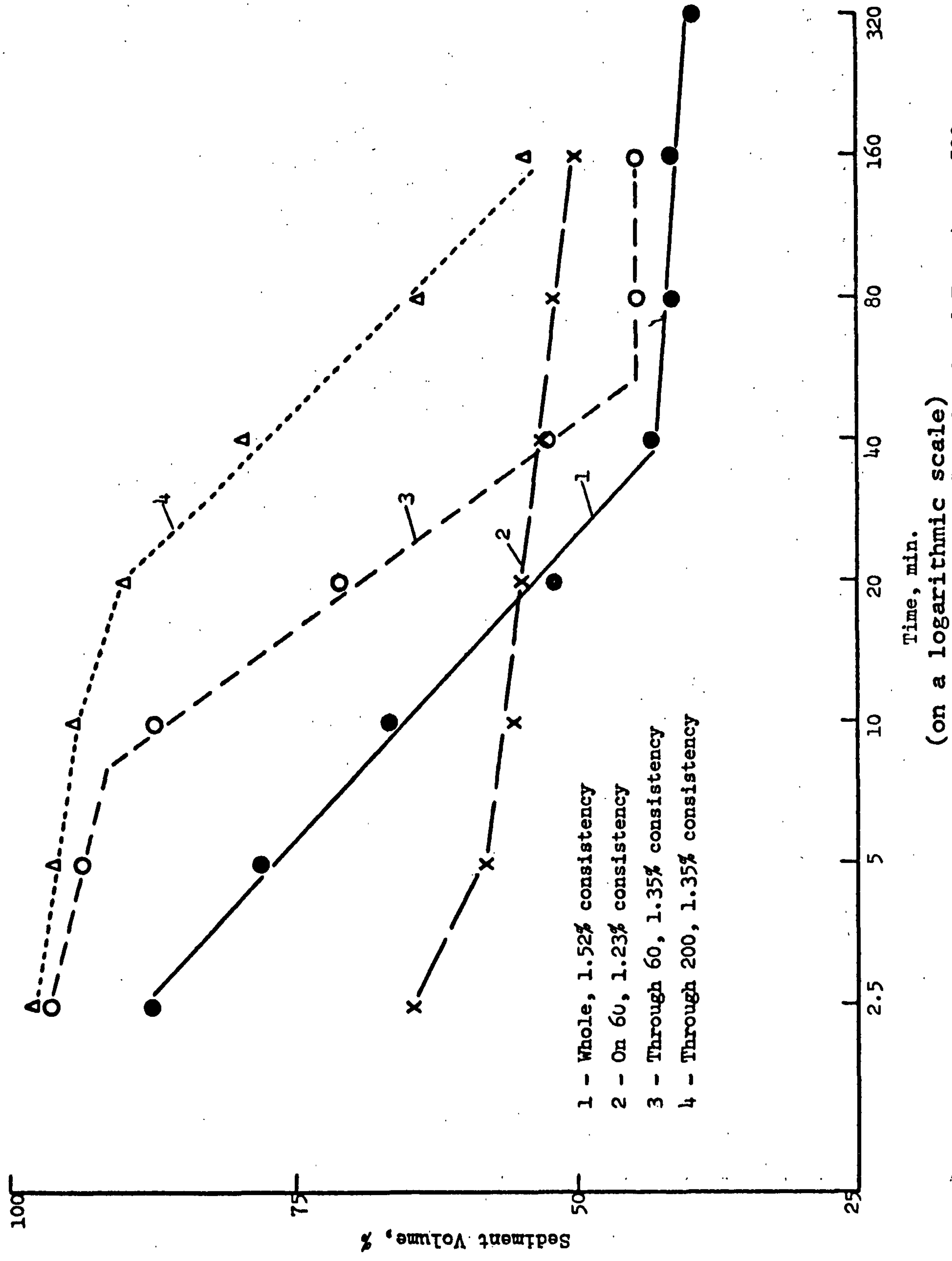



Figure 5 Centrifugal Sedimentation, Southern Pine Groundwood and Fractions, 500 r.p.m.

the separation, is closer to the behavior of the fines in the case of the sludge than in the case of the groundwood. This is perhaps what might be expected on the basis of the particle size distributions, and would suggest the importance of the "through 200" fraction in the sludge. The later stages of the sedimentation curves suggest an influence on the "on 60" fraction. The final level for the "whole" sample is closer to that of the "on 60" fraction in the case of the groundwood than in the case of the sludge.

The relatively low consistency of the final level of the "on 60" fraction for both the sludge and the groundwood suggests the occurrence of a 'brush-pile' effect limiting further separation.

It is clear from the nature of the curves that, in the region of separation covered by centrifugal sedimentation, a transition is occurring between two separation regimes. The first is a regime in which rates are determined by free fall of the particles under the influence of a density differential and a potential field. The second is one in which the compaction of the sediment is the controlling factor. And in the transition between the two regimes, the coupling of the influences of the different fractions on the behavior of the "whole" samples is quite complex.

## SEPARATION AT HIGH CONSISTENCIES

Careful examination of the results of the sedimentation studies summarized in the first four sections led to recognition that these studies cannot cover the range of consistencies which is important in practical dewatering systems. The final consistency of the sediment in all of the centrifugations does not exceed 5%. In order to explore the phenomena which dominate under conditions of practical interest, the consistency range between 10 and 30 or 40% must be accessible. An alternative instrumental approach was therefore necessary. The basic requirement was that an opportunity for drainage of interstitial water be provided. Clearly this is not possible in the usual sedimentation experiments where drainage of interstitial water is impossible.

After consideration of a number of techniques which have been used to measure the affinity of fiber systems for water, a method developed at the Institute by Thode, et al. (12), was chosen. In essence, this technique utilizes what might be called a centrifugal filtration procedure, wherein the centrifuge tube is replaced by a device which enables exposure of a pad of fiber to a centrifugal field while at the same time allowing drainage of water from the pad. The device substituted for the centrifuge tube is illustrated in Fig. 6. A specially constructed centrifuge head is available at the Institute for use with this device.

The procedure is carried out in two stages. In the first, a pad is formed by allowing a dispersion of the fiber to drain, under the influence of gravity, through a fine screen supported by the septum. The septum and the pad are then transferred to the device illustrated, the assembly is inserted into the centrifuge, and it is spun at a preselected speed for a preselected

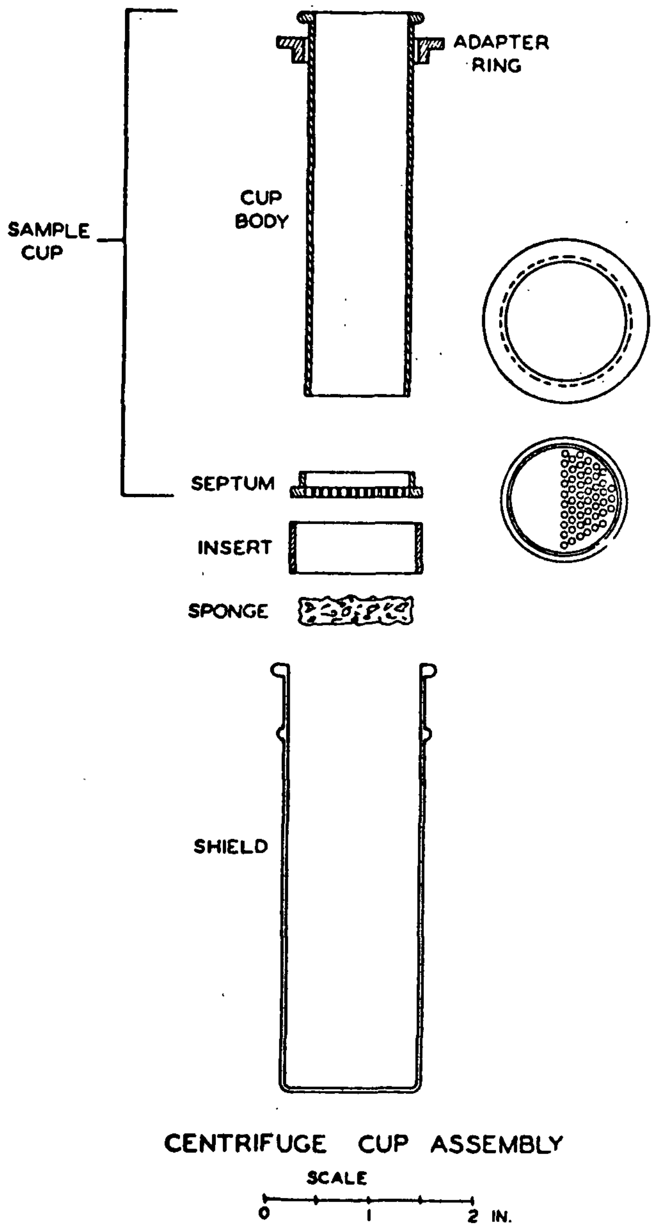



Figure 6. Centrifuge Assembly

(Not Shown in the Diagram is a Disk of 100-Mesh Bronze Screen Which is Placed Over the Septum to Prevent Loss of Fines in Routine Testing) interval of time. At the conclusion the pad is weighed, then oven-dried and weighed again. This then provides a measure of the water retained by the fiber mat against the influence of the centrifugal field, and thus a measure of the capacity of the fiber pad to bind water.

Thode, et al., defined the CWR value as: (the ratio of water content to solids content) x 100. Thus, a solids content of 25% would correspond to a CWR value of 300. In the present work the results have been reported as the final % solids.

The rotational speed used for all of the studies was 3800 r.p.m., corresponding to a relative centrifugal force (g) of 3000. Though the final solids content is known to vary with the value of g, the variation is gradual under the conditions which have been selected. Thus, as long as the conditions are maintained constant the measurements provide a sound basis for comparison of the sludges and groundwood systems.

The choice of the CWR method had another motivation, for, in addition to providing a measure of the capacity of the pad to bind water, it can provide a measure of the drainage properties of the pad. Thus, if the consistencies of the initial dispersions are kept the same, the drainage time measured during formation of the pads can be taken as a measure of the drainage properties of the pad and/or the filterability of the dispersion.

The first group of experiments involving the use of the CWR technique were directed at comparing the Sludge A-3 with the groundwood SP. The results are given in Table V, where the drainage times and the final solids contents are compared. It is clear that although the final solids contents are close in value, the dewatering properties reflected in the drainage time are quite different. The drainage time measured for the sludge is greater, by a factor of almost seven, than that measured for the groundwood. This is perhaps the first clear indication that practical dewatering problems are related to rate-determining phenomena rather than to equilibrium limitations.

TABLE V

CENTRIFUGAL WATER RETENTION

Groundwood SP & Sludge A-3

| | Final Solids, % | Drainage Time, min. |
|---|---|---|
| Groundwood SP | 26.9 | 5 |
| Sludge A-3 | 24.4 | 34 |

## SIZE EFFECTS

The next group of experiments were concerned with the behavior of different fractions of the groundwood SP. The same coarse fractions as in the sedimentation studies were used. The results are compared in Table VI. In this instance the drainage times for the "whole" and "on 60" fractions are to be compared to the "through 60" and "through 200" samples only in a qualitative way. In the latter two cases it was necessary that the pad be formed on a synthetic fabric rather than the 100-mesh screen usually used. In addition, vacuum was applied to promote drainage.

The effect of size on both drainage time and final solids content are indicated in the comparison. The two smaller fractions are more difficult to dewater by both measures of dewatering character. Their inclusion in the "whole" sample has a significant influence on both final solids content and drainage time.

TABLE VI

CENTRIFUGAL WATER RETENTION

Groundwood SP — Fractions

| | Final Solids, % | Drainage Time, min. |
|---|---|---|
| "Whole" | 26.9 | 5 |
| "On 60" | 45.5 | 2.5 |
| "Through 60"[a] | 25.3 | 8.5 |
| "Through 200"[a] | 22.0 | 40 |

[a]A synthetic fabric was used above the septum.

The most definite indication of the importance of particle size is the difference between the "on 60" and "through 200" fractions. Even though the comparison of drainage times must remain a qualitative one, it is clear that the "on 60" fraction is an easily dewatered dispersion, while the "through 200" fraction would represent a problem system comparable to the worst sludges.

## CHEMICAL EFFECTS

The results presented above indicate that the presence of fines is an important factor in determining both the drainage characteristics of the solid and the final water retention against the centrifugal field. The question arises as to whether this is primarily a size effect, or whether the higher content of hemicelluloses and pectic substances is also a factor. In a search for answers to these questions a series of experiments was undertaken focussing on the effects of chemical composition on both drainage time and centrifugal water retention.

In order to permit complete control of the chemical composition, the experiment was undertaken with samples of the groundwood pulp. The effect of lignin was first investigated by comparing a sample of the pulp as it was received with a sample which was delignified by a procedure designed to minimize the loss of carbohydrates. The delignified sample was then subjected to extractions with aqueous solvent systems of increasing capacity to solubilize the polysaccharides. A sample was also treated with pectinase. After each treatment the centrifugal water retention capacity of the fibers was measured together with the drainage time during pad formation. The results are summarized in Table VII, and discussed in detail in what follows. The extracts and the fibers were also subjected to chemical analyses after each treatment. The results of these analyses are tabulated in Appendix I.

TABLE VII

CENTRIFUGAL WATER RETENTION

Extraction and Pectinase Treatment

| | Final Solids, % | Drainage Time, min. |
|---|---|---|
| 1) Groundwood SP | 26.9 | 5 |
| 2) Holocellulose | 23.3 | 77 |
| 3) Cold water, 48 hr. | 25 | 45.6 |
| 4) Water, near boil, 3 hr. | 24.4 | 27.9 |
| 5) 0.1% NaOH, 2 hr. | 22 | 48 |
| 6) 1.0% NaOH, 2 hr. | 23.4 | 41.1 |
| 7) 2.0% NaOH, 4 hr. | 22.9 | 43.8 |
| 8) 4.0% NaOH, 20 hr. | 23.3 | 16.2 |
| 9) Pectinase treatment after cold water extraction | 24.9 | 25.1 |

<u>Lignin</u>

Most laboratory delignification processes utilize aqueous media which inevitably also remove some of the water-soluble polysaccharides during delignification. It was felt that in order to develop an accurate picture of the potential role of polysaccharides it is necessary that this loss of carbohydrates be avoided. The procedure chosen was a modification of an organic delignification procedure developed in previous work at the Institute (13-15). It is described in detail in Appendix II.

The procedure involved chlorination of the lignin by immersion of the pulp in carbon tetrachloride saturated with chlorine at 0°C. This was followed by washing with a solution of ethanolamine in ethanol. The process was repeated a number of times until a lignin content of less than 1% was achieved. The resulting pulp, designated "holocellulose," was used as the beginning material for the sequence of extractions.

Before it was subjected to the sequence of extractions, measurements of the centrifugal water retention and the drainage time were carried out on the holocellulose. The results which are included in Table VII reveal a dramatic change in the drainage characteristics as a result of delignification. Although the difference in the final solids content is not very large (26.9 for the groundwood *vs*. 23.3% for the holocellulose) the drainage time increases from 5 minutes for the groundwood to 45 minutes for the holocellulose, indicating an overall ninefold reduction in the drainage rate as a result of the delignification and the increased access of water to the hemicelluloses.

Aqueous Extractions

The first extraction carried out on the holocellulose was a cold water extraction for 48 hours. This led to a reduction in the drainage time and a higher final solids content. Sugar analyses of the holocellulose before and after extraction revealed an increase in the glucan content as a percentage of the total, indicating a reduction in the ratio of hemicelluloses to cellulose. In addition, it was found that the content of pectic substances was cut almost in half by the extraction.

The cold water-extracted sample was then subjected to extraction in water at near boiling for 3 hours. This produced a further reduction in drainage time, but also a slight reduction in final solids content. The chemical analyses revealed reduction in the content of pectic substances, as well as a lowering of the hemicellulose-to-cellulose ratio.

Pectinase Treatment

In an effort to seek out the role of pectic substances, the cold water-extracted holocellulose was treated with pectinase, an enzyme capable of hydrolyzing pectin. The effect on drainage time was of the same order as that of the hot water extraction, but the effect on final solids content was barely discernible within the limits of experimental error. The chemical analyses again revealed a reduction of the hemicellulose-to-cellulose ratio. The analysis for pectin must have been influenced by the enzyme treatment procedure because it indicated an increase in pectic substances. On the other hand, the analysis of the filtrate indicated removal of substantial amounts of pectic substances from the holocellulose. A surprising feature in the results of the chemical analyses is the clear indication that the pectinase treatment led to a reduction in the content of xylan almost equal to that measured subsequently due to the extraction with the 2% caustic solution.

Caustic Extractions

In another series of tests, entirely apart from the enzyme treatment, the hot water-extracted holocellulose was subjected, in four steps, to extraction with caustic solutions of increasing strength. The first extraction was with 0.1% caustic. This was followed by 1.0, 2.0, and 4.0% caustic in that order. Such a procedure has been shown by Thompson and coworkers to result in sequential removal of hemicelluloses of increasing resistance to hydration (16). The chemical analyses carried out in the present program supported this finding. The glucan content as a percentage of the total increased with successive extractions, and the galactan-to-mannan ratio, discussed previously (11), decreased. Analyses of the filtrates also confirmed the removal of substantial quantities of hemicelluloses.

The effect of the first three caustic extractions on the centrifugal water retention and the drainage time were rather surprising. As indicated in Table VII, the drainage time increased relative to its value for the hot water-extracted holocellulose, while the final solids content decreased. It would appear that the effect of the caustic solutions in swelling the remaining hemicelluloses and cellulose more than compensates for the reduction in the content of hemicelluloses. That the removal of the hemicelluloses remains an important factor is indicated by the value of the drainage time recorded after the 4.0% caustic extraction. Here again, however, the final solids content remains quite low, and, within experimental error, the same as for the unextracted holocellulose.

## OTHER STUDIES

In an effort to develop additional information to aid interpretation of the results described in the previous section a number of additional studies were undertaken. These included Scanning Electron Microscopic examination of a number of samples, measurements of isotope exchange capacities to establish accessibility to hydration, and exploration of the effect of modified clays on the drainage behavior of the holocellulose dispersions. All of these studies contributed to developing a clearer picture of the phenomena of concern.

### ISOTOPE EXCHANGE STUDIES

One of the techniques which has been used quite frequently to measure the accessibility of cellulosic fibers to hydration is the deuterium exchange technique (17). The fibrous sample is exposed to deuterium oxide for a period of time, and the amount of exchange between deuterium and hydrogen is measured by monitoring any one of a number of properties sensitive to the difference between deuterium and hydrogen. In the present instance the property chosen was the intensity of the hydroxyl stretching band in the infrared spectrum of the sample. By immersing the sample in deuterium oxide for a suitable interval, then freeze drying it, and repeating the process a number of times, it is possible to insure that all hydroxyl groups which are accessible are converted from OH groups to OD groups. This results in the appearance of a new band in the infrared spectrum because the higher reduced-mass of the deuterated hydroxyl group results in a lower characteristic frequency of vibration of the bond. The new frequency is sufficiently different that the new band is very well resolved. It occurs at 2482 $cm.^{-1}$ To provide an inner reference in each sample the CH stretching vibration is also measured. Since the hydrogen in CH bonds does not exchange the intensity of this band is unaffected by the deuteration. The ratio of the intensities of the OD and CH bands can then be taken as a measure of the amount of hydroxyl group that has undergone deuteration.

The deuterium exchange technique was applied to two groups of samples. The results are given in Table VIII. The first group involves a comparison of a cold water extracted sample of the holocellulose with a sample extracted with the 4.0% caustic. The increase in the OD/CH ratio upon extraction with the caustic is an indication that a greater number of hydroxyl groups is accessible to hydration in that sample. The only way in which this could have come about, in spite of the removal of significant amounts of hemicelluloses, all of which would be accessible to hydration, is through much greater fibrillation of the 4.0% caustic-extracted sample. This observation is consistent with the results of the SEM examination of these particular samples to be discussed below.

TABLE VIII

ISOTOPE EXCHANGE MEASUREMENTS ON HOLOCELLULOSE

| | Ratio of Intensities of the OD and CH Bands (OD/CH) |
|---|---|
| Group 1 | |
| Cold water extracted | 0.59 |
| 4.0% NaOH extracted | 0.69 |
| Group 2 | |
| Holocellulose | 0.78 |
| Cold water extracted | 0.93 |
| Hot water extracted | 0.93 |

The second group of samples subjected to deuterium exchange involves comparison of the untreated holocellulose with the cold water and with the hot water-extracted samples. In this comparison it is clear that the extraction with cold water has the same effect relative to the holocellulose as the caustic extraction relative to the cold water-extracted sample. The hot water-extracted sample appears unchanged relative to the cold water-extracted sample.

It should be noted that the two groups of samples are not comparable on an absolute basis because the first group was air-dried at one point prior to deuteration, while the second group was freeze dried at all points during preparation prior to deuteration. It is well known that the water drying of fibers results in irreversible changes in structure, and that this change is minimized when fibers are freeze dried. Evidence for this effect will be noted later in discussion of the SEM work.

EFFECTS OF MODIFIED CLAYS

Recognition of the importance of the polysaccharides in determining the behavior of sludges led to comparisons with other natural systems in which polysaccharide exteriors play fundamental roles. It is well known that interactions of polysaccharide components with amine-containing proteins play an important role in the antigen-antibody reaction which usually results in precipitation of the antigen-antibody complex. It was thought worthwhile, therefore, to carry out preliminary exploration of the possible interactions between the sludge constituents and suitable amine-containing species.

Candidate species which suggested themselves included amine-modified clays which are particulate and contain the quaternary amine functionalities of interest. Dispersions of the modified clays were added to dispersions of the holocellulose and of the groundwood SP and the drainage times measured. The results are shown in Table IX. It is clear that the clays resulted in measurable reduction in drainage times.

TABLE IX

EFFECT OF MODIFIED CLAY ADDITION ON DRAINAGE TIME

| Amount of Clay Added as % of Pulp | Drainage Time, min. | |
|---|---|---|
| | Groundwood SP | Holocellulose |
| 0 | 6.5 | 95.5 |
| 16.7 | 5.3 | 66.6 |
| 33.3 | 4.9 | 44.6 |
| 66.7 | 5.1 | 45.5 |
| 100 | 6.1 | 38.2 |

In order to establish whether the effect is simply due to the presence of inorganic inert particles or whether the amine functionalities are indeed involved, a similar series of experiments were carried out with the holocellulose utilizing unmodified clays some of which were of the same base material as the modified clays. The effect of the unmodified clays was in every instance a dramatic increase in drainage time. Indeed, in every case after five hours less than half the dispersion had passed through the septum so the experiments were discontinued. Thus, there is very little doubt that the amine modification is an important factor in the action of the clays.

In an effort to understand the mechanism of action of the modified clays some of the pads obtained during the drainage time measurements were examined in the Scanning Electron Microscope. The photomicrographs will be discussed below with other SEM work.

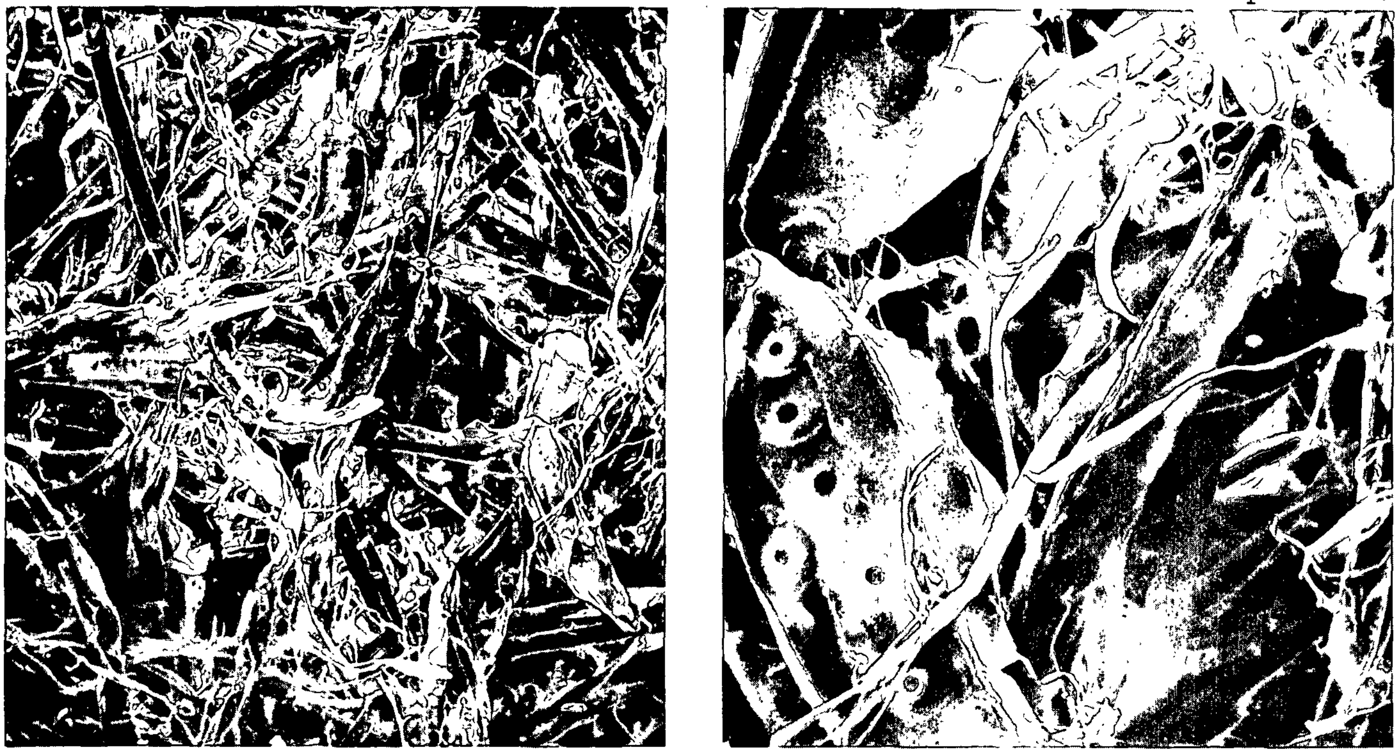
SCANNING ELECTRON MICROSCOPE

The Scanning Electron Microscope (SEM) has been acquired by the Institute since submission of the proposal for this work, so that its use had not been envisioned at that time. Since its acquisition it has been used whenever it seemed capable of adding to the information available on the structure of the sludges or the model systems. It has provided an important additional dimension complementing information available from other sources. Although it will be presented here in terms of contrasts between photomicrographs of different types of samples, the overall view of the samples provided by direct examination in the SEM is a more comprehensive one. For example, it is possible to scan a considerable area of a sample in order to develop an appreciation for its uniformity. Also, it is possible to select a specific area and vary the magnification continuously so that a particular feature can be viewed in relation to its environment at a number of levels. In what follows, the discussion will thus be, in part, an interpretation of what has been revealed in direct examination, rather than confined to information contained in the photomicrographs which have been chosen for reproduction. In most instances the samples used for examination were the pads formed in the course of the CWR measurements after they had been oven-dried. One of the many advantages of the SEM is the possibility of examining such samples directly without elaborate preparative procedures other than the metallic coating by vaporization, a relatively routine procedure requiring only a few minutes.

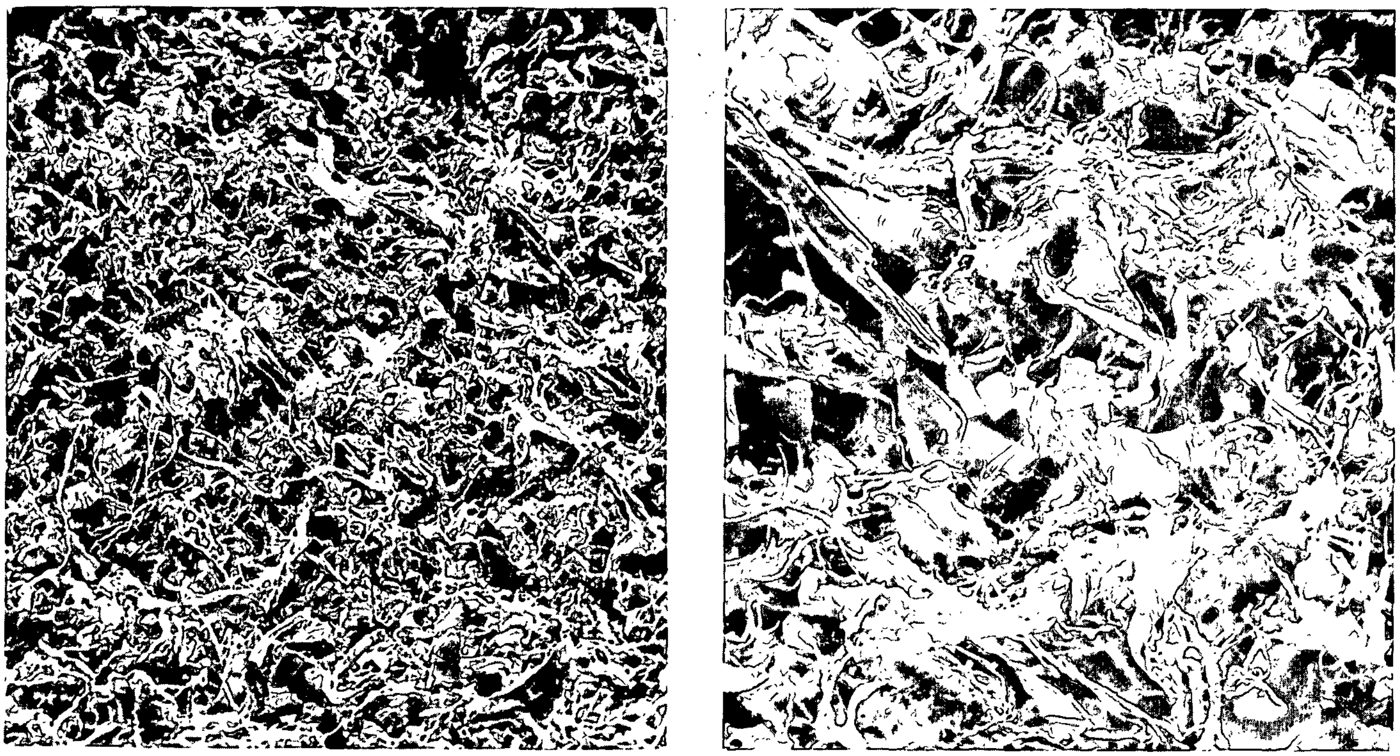
## SIZE EFFECTS

A dramatic illustration of the power of the SEM is seen in Fig. 7, which includes photomicrographs at 160X and 500X of the "on 60" and "through 200" fractions of the groundwood SP. These views are of the surfaces of the pads and give an indication of the difference which caused the differences in final solids content and in drainage time. It is clear that the "through 200" fraction is capable of much greater compaction resulting in far smaller pore sizes. The smaller pore size in turn leads to both greater resistance to flow, hence the longer drainage time, and greater retention of water by capillary action, hence the lower final solids content. It is also clear that the "through 200" fraction consists primarily of fine fragments of fibers, while the "on 60" fraction includes many clearly recognizable features of whole fibers.

Another informative comparison is shown in Fig. 8. Here photomicrographs of Sludge A-3 are compared with photomicrographs of the "through 200" fraction of the groundwood SP. The 160X micrographs indicate that the fragment size is quite comparable in the two samples. The micrographs at higher magnification reveal some differences in that the "through 200" sample of the groundwood seems to have retained its fibrillar structure much more than the sludge. The difference is in part an artifact of the drying procedure. The sludge sample was dried over $P_2O_5$ at room temperature, while the "through 200" fraction was oven-dried. Drying at room temperature results in greater collapse of the fibrillar structure than oven-drying. Oven-drying in turn leads to greater collapse of fibrillar structure than freeze drying.

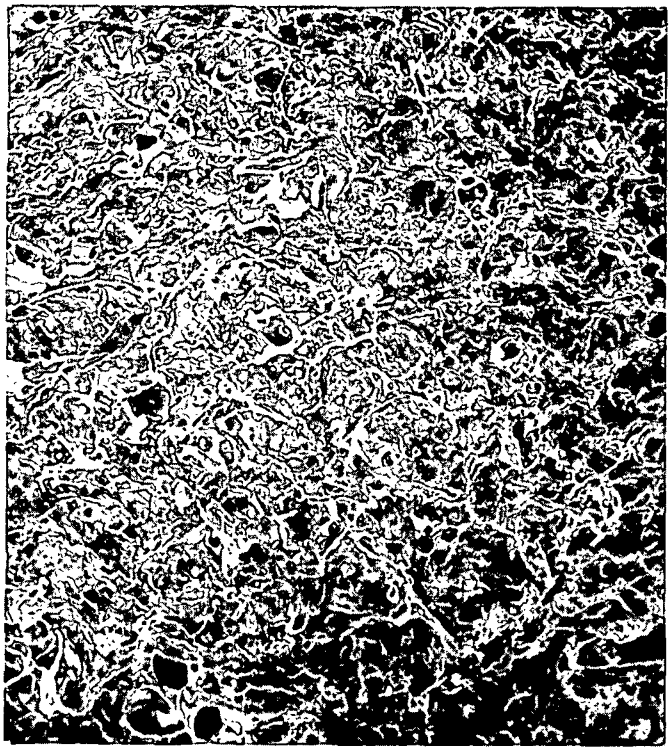


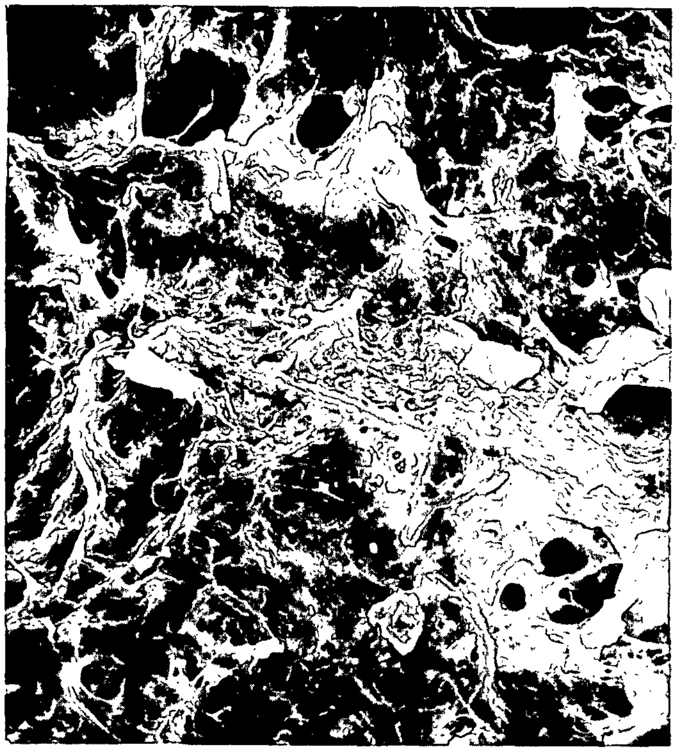
160X Groundwood SP "on 60" 500X



160X Groundwood SP "through 200" 500X

Figure 7. Photomicrographs at 160X and 500X of the "on 60" and "Through 200" Fractions of the Groundwood SP





160X Sludge A-3 1000X

160X Groundwood SP "through 200" 1000X

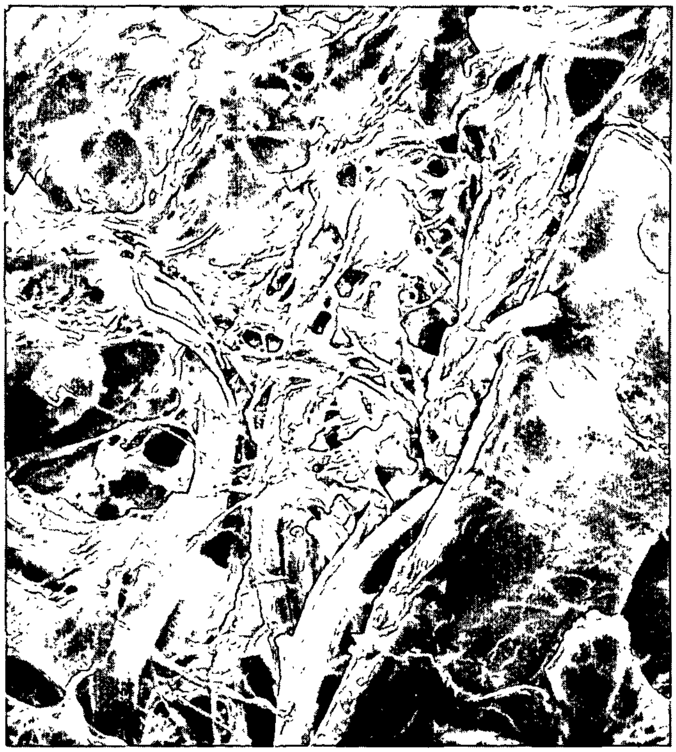
Figure 8. Comparison of Sludge A-3 Photomicrographs with the "Through 200" Fraction of Groundwood SP

EXTRACTION

To explore further the effect of extraction of the polysaccharides on the structure of the model system, the pads formed in the CWR test after each of the extraction stages were examined with the SEM. In this case the differences were evident only at 1000X magnification. Four photomicrographs are shown in Fig. 9: (a) is a micrograph of the holocellulose, (b) is the pulp after cold water extraction, (c) is after treatment with pectinase, and (d) after the extraction with 4.0% caustic. The progress in the degree of fibrillation from (a) to (b) to (c) and from (a) to (b) to (d) is quite clear. Whether the degree of fibrillation of (c) or (d) is greater is not as clear. The increased fibrillation resulting from extraction of the hemicelluloses and the pectin is correlated with increased porosity, a reduced resistance to flow, and hence a shorter drainage time. On the other hand, it is clear that the dimensions of the fibrils are such that the new pores are quite small and thus capable of retaining water by capillary action. Hence, the relative invariance of the final solids content. It should be noted that although they have not been reproduced here, the photomicrographs of the pulp after the extraction stages intermediate between cold water and 4.0% caustic, also show the progressive increase in fibrillation.

DRYING

In order to develop an understanding of the effects of drying on the appearance of the samples in the SEM photomicrographs a comparison was made between two samples of groundwood SP, one of which had been freeze-dried, the other vacuum dried over $P_2O_5$ at room temperature. The micrographs are compared in Fig. 10. It is clear that the sample dried at room temperature



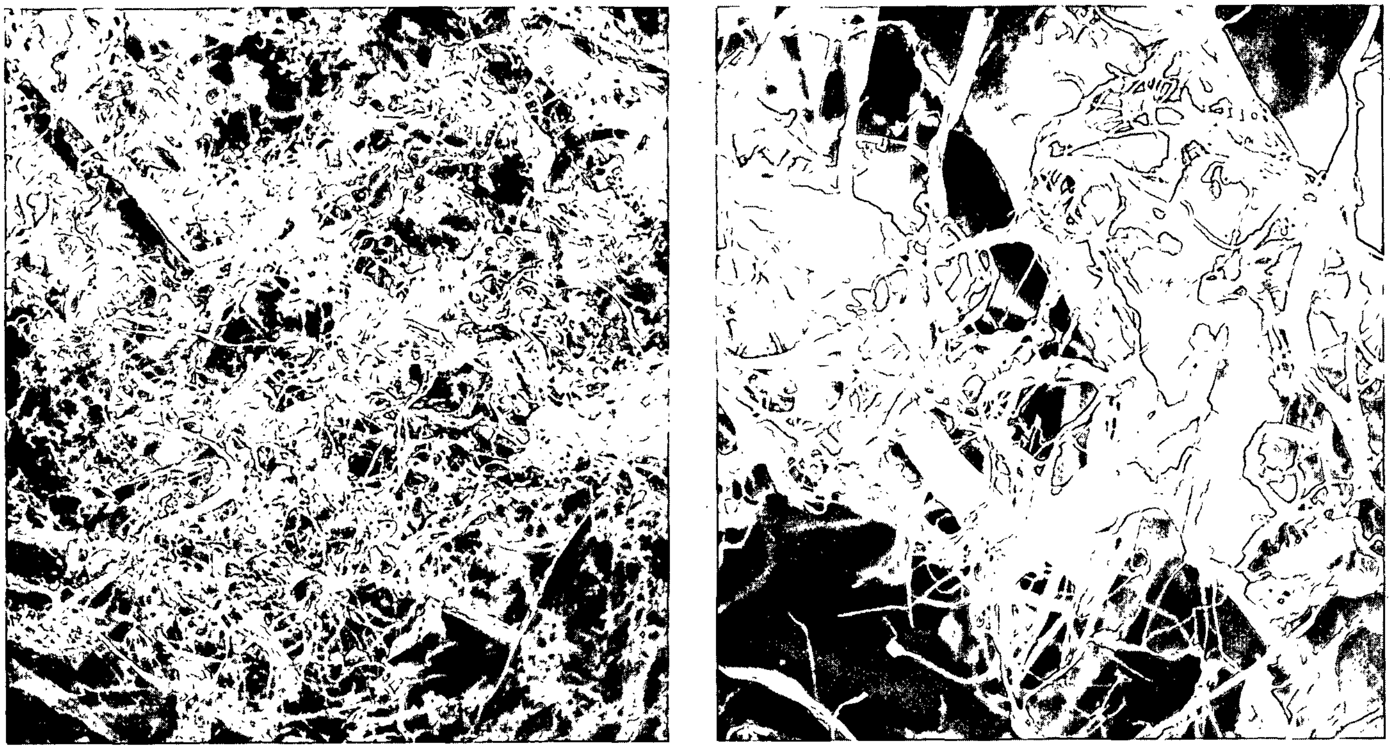
1000X Holocellulose A

1000X Cold Water Extracted B

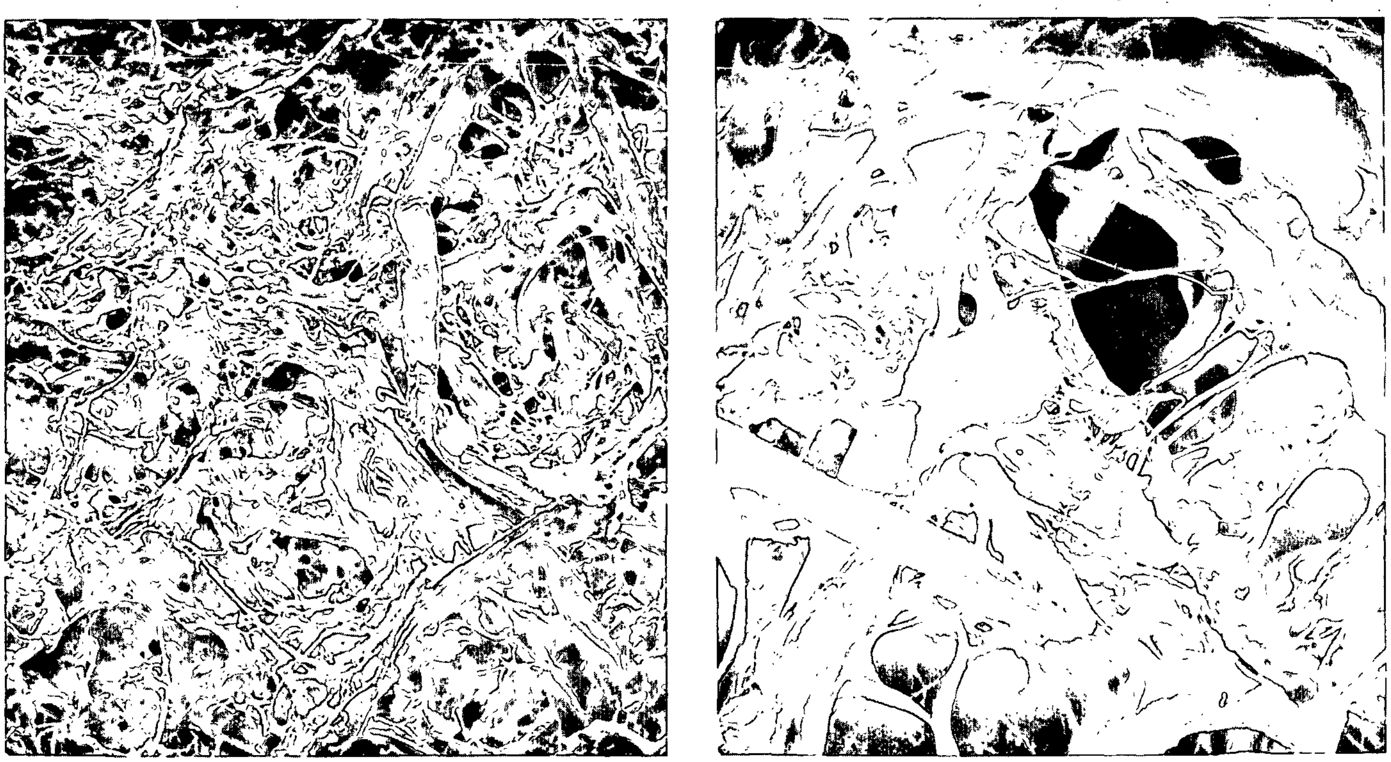
1000X Pectinase Treated C

1000X 4% NaOH Extracted D

Figure 9. Effect of Extraction of the Polysaccharides on the Structure of the Model System



160X Groundwood SP, freeze dried 1000X



160X Groundwood SP, vacuum dried over $P_2O_5$ 1000X

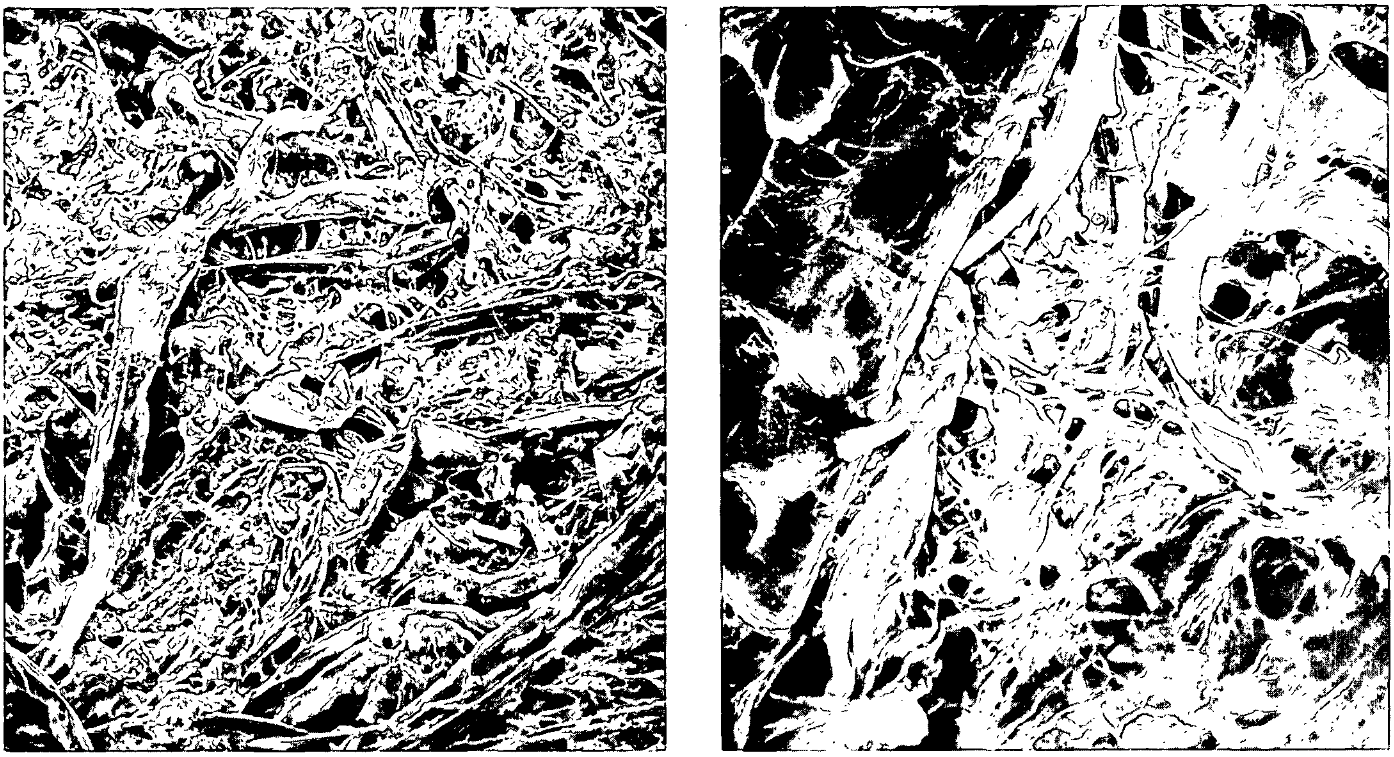
Figure 10. Effects of Drying on Appearance of Samples

has experienced a much greater degree of collapse of its fibrillar structure. This phenomenon is a consequence of the action of capillary forces during drying, and is related to the surface tension of the fluid from which the sample is dried. In freeze drying the capillary forces do not have an opportunity to act so that the structure of the material undergoing drying is preserved to a much greater degree.

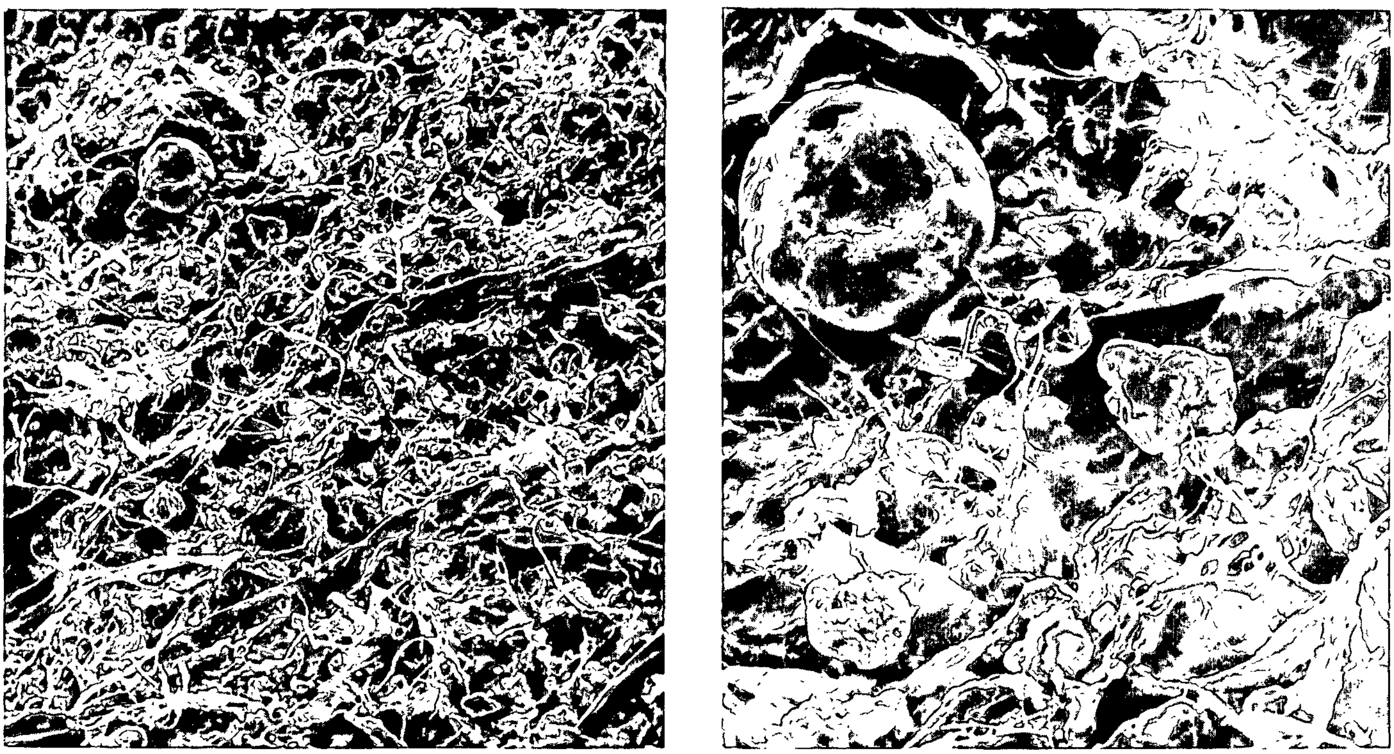
In the comparisons reported in the present work, the drying procedures have been identical except where it has been so noted.

## MODIFIED CLAY ADDITION

As noted above some of the pads formed during the measurements of the effect of amine-modified clays were subjected to examination in the SEM. The photomicrographs compared in Fig. 11 are of the holocellulose and of the holocellulose with an equal portion of the amine-modified clay added. Though the high magnification micrographs differ in magnification by a factor of two, it remains clear that the effect of clay is to provide a site for the deposition of the fibrils which in the absence of the clay seem to bridge the gap between one fiber fragment and another. Thus, the porosity of the pad incorporating clay seems to be greater than that of the pad made from the holocellulose alone.



160X Holocellulose 1000X



160X Holocellulose Plus Amine Modified Clay 500X

Figure 11. Effect of Amine-Modified Clays on the Model Systems

## DISCUSSION

Before discussing the interpretation of the experimental phases of the program it is useful to consider the possible relevance of the notions previously suggested by Gehm (1) in efforts to interpret the behavior of sludges. He found it useful to introduce the notion that water exists in three phases in the hydrous sludges. He spoke of free water, interstitial water, and water of imbibition. He writes:

> "In respect to the water phases, the free water is readily removable, the interstitial water difficult to remove, and the water of imbibition cannot be separated at all by mechanical methods, being part of the crystal lattice formed by the colloidal sols."

While the terminology introduced by Gehm is valuable and descriptive, his use of the term "phases" to describe the different levels of association of water with the constituents of the sludges can lead to some confusion, for it implies different types of association at the molecular level. From the applications point of view it implies that the removal of the interstitial water would represent approach to a state which is thermodynamically distinct from one in which only the free water had been removed. This in turn could imply that the limits in practical dewatering operations are determined by thermodynamic constraints. One of the primary conclusions of the present work is that the limits on practical dewatering systems are set by rate-determining phenomena rather than by thermodynamic limits. For this reason the terminology introduced by Gehm will not be used. As noted in the introduction, the term hydrogel has also been avoided for similar reasons.

The primary conclusion indicated above is based on the observation that the solids levels attained in the centrifugal water-retention measurements are of the same order of magnitude as those often desired in practical dewatering operations. The attainability of these levels in an ordinary laboratory centrifuge is an indication that the water being separated is not associated at the molecular level in any way that differs from free water. Although centrifugal fields are capable of bringing about chemical potential gradients, only in the ultracentrifuge are these finite and observable. Any separation attainable in a laboratory centrifuge must be interpreted only in terms of mechanical forces based on differences in specific gravity.

Implicit in the above paragraph is the conclusion that in all of the experimental separations carried out in the present program the mechanisms which are dominant must be understood in mechanical terms. The effects of chemical composition can be comprehended therefore only to the extent that they can be interpreted mechanically.

The experimental separations described in previous sections fall into two categories, each of which can be related to a different stage in dewatering operations and each of which is dominated by a different set of mechanical factors. The sedimentation studies were concerned with the effects of constitutional variables on sedimentation behavior where the rates of separation are determined primarily by particle size and the density difference, and where each particle is removed from the influence of other particles. The centrifugal water retention measurements were concerned with separations that involve drainage of water through interstices once contact between the particles has occurred. In this case the separation rates are determined by factors which determine the size of passages available for flow. Among these factors are not only the obvious ones such as particle size and particle size distribution, but also less obvious ones related to the chemical composition such as the deformability and conformability[3] of the particles. These determine the degree to which compaction can result in reducing the porosity of a fibrous mass.

SEDIMENTATION STUDIES

The results of the sedimentation investigations provide a basis for understanding some of the factors which determine separation rates in clarification operations. They also point out an important limit on the application of centrifuges in dewatering operations.

Since the driving force in the operation of a clarifier is the gravitational potential acting on a density differential between the components to be separated, the same consitutional factors which determine the response of a dispersion to the gravitational field also determine its response to a centrifugal field.

The sedimentation studies described in the "Characterization" and "Separation at Low Consistencies" sections indicate that two major factors determine the response of sludge components to a potential field. These are the constitutional variables of particle size and chemical composition.

[3] The difference between deformability and conformability is perhaps best illustrated by the difference between the deformation properties of a dry and a wet noodle.

The particle size distribution enters in that it indicates what fraction of the whole sludge has a particular surface-to-volume ratio. This ratio in turn determines the ratio of viscous drag forces to inertial forces in the potential field, and thus determines the rate of "fall" of the particle through the water in response to the potential field. It is not surprising, therefore, that the "through 200" fraction was the slowest separating of the fractions.

The chemical composition enters into determination of the sedimentation rates indirectly in that it determines the density differential between the particles and the water. In the present case, the major variation with composition is related to the effect of composition on the degree to which the fibrous tissue swells. The greater the degree of swelling, the more closely does the density of the fiber approach that of water, and the smaller is the differential in the specific gravity between the fibers and the water. It is thus probable that the higher content of pectins and hemicelluloses in the "through 200" fraction magnifies the effect of size in slowing down the separation rate in comparison to the larger size fractions.

The other aspect of the sedimentation measurements which is worthy of note, is the observation of the limits approached in the different sedimentations. That the limit is determined by particle size is indicated by the observation that the limit is highest for the "on 60" fraction. Although in Fig. 4 and 5 the "through 200" fraction appears not to have reached a limit, a plot on a linear time scale shows a change in slope indicating interparticle contact.

The observation of the limits due to interparticle contact at relatively low consistencies is quite relevant to evaluation of centrifuges as practical dewatering devices. It is clear that at higher consistencies than the limits indicated, that is, at consistencies higher than 4 or 5%, the centrifuge can dewater a sludge only to the extent that it can bring about compaction or compression of the solids. That is, it has to function as a press.

This observation may explain why efforts to dewater sludges by continuous centrifugation have often encountered significant complications.

## CENTRIFUGAL WATER RETENTION STUDIES

The centrifugal water retention studies are more directly related to the problem area in sludge dewatering than the sedimentation studies. Most of the difficulty is usually associated with dewatering from a consistency of about 5% to one of about 30%. In the course of this separation large amounts of water must be removed from the solids. Though, of course, proper operation of clarifiers is essential to success in the later stages, the basic principles of sedimentation in the "free fall" region are well understood, so that little guess work is involved in the design of the necessary equipment. The design of dewatering equipment for the stages which occur after the first contact between the particles is much less straightforward.

The most common procedures for accomplishing the desired separations are filtration and centrifugation. Both of these procedures are related to aspects of the centrifugal water retention studies described in the section on Separation at High Consistencies. The drainage time measured during the formation of the pad is clearly related to the parameters which would determine rates of filtration. A little less directly these same parameters would influence the rate of compaction of the solids in a centrifuge where removal of interstitial water can be the rate-determining step.

The final solids content, although it is a measure of the capacity of the centrifugal field to expel water that is held in the interstices of the pad, is not directly related to the usual centrifuge dewatering. This is because the centrifugal water retention measurement reflects the properties of a two-phase system, and is rather a measure of the action of the capillary forces and the true molecular hydration of the fibers.

Although, when the whole range of values is considered, it appears that samples which had a long drainage time also had a lower final solids content, more careful examination indicates that there is no clear correlation between the two. This is consistent with the fact that the drainage time is a reflection of a transient hydrodynamic phenomenon, while the final solids content is determined by equilibrium structural and constitutional characteristics of the fiber pads. It seems logical, therefore, to discuss separately the influence of the constitutional variables on the two different measures of pad properties.

## Final Solids Content

The effects of particle size on the final solids content can be understood in terms of two different factors. The first, and probably the dominant one, is the size of the interstices and their capacity to retain water against the centrifugal field through capillary action. The relation between particle size and pore size is clearly illustrated in the SEM photomicrographs in Fig. 7. The "through 200" fraction has compacted into a pad of much smaller pore sizes than the "on 60" fraction. The second factor is the content of swellable polysaccharides which can bind water at a molecular level. It is probable that both factors are important in the difference between the final solids content of the "on 60" fraction (45.5%) and that of the "through 200" fraction (22%). This also correlates with prior knowledge of the influence of large-fiber fraction on ease of dewatering.

The results of the extraction studies are rather more complex than those of the particle size studies. Here it is clear that in some instances, while the extraction has reduced drainage time significantly, it has also resulted in a reduction of the final solids content. This appears related to two effects of the extraction which proceed simultaneously. On the one hand, the removal of swellable polysaccharides, including hemicelluloses and pectin, reduces the content of material which can bind water at the molecular level, and on the other hand the removal of these substances seems to result in greater fibrillation and an increase in the number of fine capillaries in the pad which are capable of holding water by capillary action. This was perhaps best illustrated in the results of the isotope exchange studies wherein extraction with caustic as well as extraction with water resulted in an increase in the total fraction of hydroxyl groups which are accessible for deuteration. This effect is also clear in the SEM micrographs where a greater degree of fine fibrillation was observed in the extracted samples than in the original holocellulose.

When one considers, on the one hand, how little difference in final solids content is observed on going from the original holocellulose to the pulp extracted with 4% caustic, and on the other hand that the drainage time for the latter is approximately one fifth that for the former, it lends credence to the conclusion, set forth at the beginning of this discussion, that the real problems in dewatering are rooted in rate-determining phenomena rather than in the attainable limit values.

## Drainage Time

The drainage time is the measure most directly related to dewatering behavior. This is particularly so in the case of filtration systems, although as noted previously the drainage time can be taken as a general measure of the drainage characteristics of the solid mass once interparticle contact is established.

The effect of constitutional variables on the drainage time can best be understood in terms of their effects on porosity. To a first approximation, it seems fair to assume that the hydrodynamic variables, other than pore size, are unchanged by the types of variations in the constitutional variables which have been explored. Thus, only variations in pore sizes need be considered.

The effect of particle size on pore size has already been considered in discussing the final solids content and the photomicrographs in Fig. 7. The much smaller pore size of the "through 200" fraction is no doubt the main factor in its long drainage time relative to the "through 60" and "on 60" fractions.

The effect of extraction on the drainage time is perhaps the most direct evidence for the role of the swellable polysaccharides in dewatering problems. The reduction in drainage time with cold and hot water extraction reflects two effects of the extractions which complement each other. On the one hand, removal of the polysaccharides increases the fibrillation and hence the porosity; on the other hand, their removal reduces the water-swollen tissues and hence reduces the conformability of the fibers. This in turn limits the degree to which compaction of the fiber pad can bring about sealing of the interstices.

The effect of the pectinase treatment can be understood in terms which parallel those outlined above for the water extraction. The effect of removal of the pectin by enzymatic hydrolysis seems to be quite similar to that of hot water extraction.

The effect of the weaker caustic solutions in increasing the drainage time seemed quite strange at first, but it can be understood in terms of a swelling of some of the tissues not normally swollen in water. This then would tend to increase the conformability of the particles and compensate for the effect of the removal of the hemicelluloses.

The most convincing evidence for the overall influence of the polysaccharides is the comparison of the original holopulp with the 4% caustic-extracted pulp. Here it is clear that the fivefold reduction in the drainage time is a consequence of removal of the hemicelluloses and the pectin. This observation is consistent with the knowledge that sludges from fragments of chemical pulps, which contain fewer hemicelluloses, are much easier to dewater.

## ACTION OF CLAYS

It is difficult to comment extensively on the action of the clays because the experiments were preliminary in nature and intended to explore the value of the analogy with the antigen-antibody reaction. As noted in the discussion of the SEM photomicrographs it does appear that an influence of the clays is an increased porosity of the pads. The considerable increase in the drainage time with the unmodified clays suggest that the amine functionalities are important and that further exploration of the analogy with the antigen-antibody reaction is worthwhile.

## CHEMICAL DIFFERENTIATION WITH GRINDING

It seems appropriate to comment briefly on the observation that sugar analysis and lignin content vary significantly with particle size. The results are consistent with past studies of the variation of composition with particle size (18). In those studies, however, the analyses of the pentosans were incomplete, and thus there were no indications of the changing nature of the hemicelluloses.

In search of a rationalization of this effect, it might be noted that initial separation of the fibers from the wood by grinding is inevitably followed by additional fragmentation. The fragments consisting primarily of cellulosic tissue are likely to undergo less additional breakage than fragments consisting primarily of fiber exteriors rich in hemicelluloses and lignin.

## DEWATERING MECHANISMS

The picture which emerges from the above discussion is one of dominance of the drainage characteristics in any effort to dewater dispersions beyond the 5% solids level. The drainage characteristics are in turn controlled to a large extent by the porosity of the solid mass once the interparticle contact is established. The influence of the constitutional variables on dewatering characteristics has thus been interpreted primarily in terms of their influence on porosity. With this background it is worthwhile to consider whether the interpretations developed can provide a basis for understanding processes which are known to enhance dewatering behavior.

The processes which have been discussed most often fall into two classes. The first is based on addition to the sludge of particulate matter which alters the structure of the compacted solid mass enough to change its drainage characteristics. Among the species which have been used successfully are the modified clays discussed above, bark fines and fibers (19), and pulverized coal (3). Of these, only the bark addition is known to be used in a mill system. The second class of processes are those which involve only physical treatments of the sludge. These include heat treatment and freezing. The heat treatment has been investigated and found successful for biological sludges (2, 20) and for primary sludges (21) from pulp and paper mills. Freezing has also been shown to be effective in improving dewaterability of primary sludges (19, 21). These physical methods are not in common use in commercial installations, however, because they are not well enough understood to permit confident design of operating systems. Since their primary requirement is power they can become prohibitively expensive if not properly designed or if they are not efficiently operated.

ADDITION OF PARTICULATES

The addition of particulate matter that has constitutional properties very different from those of the sludge fibers can clearly bring about significant changes in the porosity of the compacted solid mass. The mechanism of action of the modified clay particles has been adequately discussed above in terms of the effect of the clays on the fibrils and on the overall porosity of the fiber pads. The fibers which are used in the commercial installation referred to above are bark fines which probably provide porous channels in the solid mass. Their action can clearly be understood in terms of analogy with the effect of the "on 60" fraction on the drainage time for the groundwood pulp. The pulverized coal could act in a manner analogous with that of the clays. Clearly the surface properties of the coal must be an important factor in its effect on the drainage characteristics of the sludge.

In summary, it can be stated that the addition of particulate matter can result in enhancement of the dewatering rates if the constitutional properties of the added particles complement those of the sludge to create a more porous solid compact. Better understanding of the nature of the interaction could permit development of economical processes utilizing this path to dewatering.

PHYSICAL TREATMENTS

In order to discuss possible mechanisms for the action of heat treatment or freezing it is necessary to consider the history of groundwood components in the sludges. In the Introduction it was noted that one of the distinguishing features of groundwood fines, in comparison to fines from chemical pulps, is that they have not been subjected to severe extractive conditions and that this is why they retain a substantial portion of their original hemicelluloses. Another distinguishing feature which must now be considered is that generally the fines from groundwood have not experienced extreme temperatures. At the submicroscopic and molecular level therefore the groundwood fines should not differ from their state in the wood. There are good reasons to believe that either extreme of temperature can bring about irreversible changes in this structure. These irreversible changes are probably important factors in the change in dewatering properties upon exposure to either extreme of temperature.

Freezing

In order to understand the effect of freezing on the structure of a fragment of groundwood two important pieces of information must be kept in mind. The first is that most of the organic matter is polymeric in nature, and that therefore it can bring about only small amounts of depression of the freezing point. The second is that the polymeric organic matter cannot enter into a eutectic with water. The consequence of these two realities is that, when a fragment of groundwood is frozen, a separation into two phases must occur at the microscopic and submicroscopic levels. One phase is the frozen solid water, the other is the amorphous organic matter. The separation brings about irreversible changes in the structure of the organic matter, since for the first time since its biosynthesis it has been dehydrated. What happens when the fragment is thawed depends on the capacity of the water to diffuse again into the structures from which it has been excluded by freezing. Though very little is known of the hydration characteristics of the polysaccharides at low temperature, it is generally true that once dehydrated from their native state they can never again be rehydrated to the same level. Thus, their resistance to diffusion will remain high. The overall effect then favors continued separation of the water from the organic tissue. The stage is thus set for a mechanical operation to separate the two phases. This then is the probable basis for the "phenomenal" success of the freezing process described in (19). To relate it to the earlier discussions it might be said that the freezing process brings about irreversible changes in the relevant constitutional properties of the sludge components.

## Heat Treatment

There is now a substantial literature on the irreversible changes which occur in the cellulose fiber when it is first exposed to high temperatures. Much of the published work has been concerned with the changes in the immature cotton fiber when it is first dried or dehydrated (22). Recently, however, a thesis has been completed at the Institute (23) which demonstrated that similar types of changes occur in woody tissue. A substantial irreversible change occurs during the first heating cycle. It is not at all unreasonable to expect that groundwood fines in the sludges which are of concern here undergo similar types of changes when they are subjected to heat treatments, and that these changes may be a factor in the action of the heat treatment to enhance dewatering of the sludge.

That the effect may be closely related to the polysaccharide nature of the tissue is suggested by the solution properties of polysaccharides. It is reasonably well established that many polysaccharides and some related polymers have solution properties which have a dependence on temperature which is the reverse of the usual one. That is they are less soluble in hot water than in cold water. Some in fact are soluble only in cold water and precipitate on heating (24). A similar phenomenon may be involved in the effect of heat on the cellulosic fiber which has never been dried. This is no doubt related to the class of phenomena involved in the denaturation of living organic matter by heat. Though it is well established that the solution properties of the polymeric organic materials which make up the living tissue are a factor in the denaturation process, the solution properties themselves are complex and not well understood.

In summary, then, it may be said that the effect of heat on the fragments of groundwood can be understood in terms of denaturation. The denaturation in turn can be regarded as leading to important changes in the constitutional variables of the sludge, and hence to the dewatering characteristics.

# FUTURE DIRECTIONS

The work reported above has established some basic relationships between the constitution of the sludges and their dewatering behavior. This can be regarded as a suitable foundation for further investigations of sludge treatments structured in relation to the different options for sludge disposal available to individual mills. The types of treatment which are possible include addition of particulates, physical treatments such as heating or freezing, and chemical treatment or extraction. The disposal options available, listed in order of value recovered, are: recycling, incineration, and landfill. Landfill is clearly a total loss to the manufacturing operation. Incineration permits recovery of the energy content only, while recycling results in recovery of materials. Each of these options places different constraints on the choice of treatment methods for the sludges.

For recycling into paper or board products the major requirement is that the drainage properties of the sludge be modified so that they do not bring about intolerable changes in the drainage characteristics of the furnish into which the sludge is recycled. Since recycling represents an opportunity for some recovery of function it provides greater latitude in choice of approaches. For example, if addition of particulate matter is the method chosen, both the fiber in the sludge and the added particles can be regarded as fillers. Even if physical or chemical treatment were used to prepare the sludge for recycling the recovery of function would reduce the loss represented by the cost of conditioning.

Incineration places additional constraints on the available options. Clearly the approach chosen must result in a product which will support combustion. If particulate addition is chosen the added particles may need to be combustible. If physical or chemical treatments are chosen they will have to be undertaken under greater economic constraint than in the case of recycling, for in incineration only the energy of the organic solids in the sludge is recovered.

Landfill disposal represents a total loss of value of both the sludge and whatever agents are utilized in dewatering. Thus, it places the greatest number of constraints on the choice of sludge dewatering procedures.

In this light a logical extension of the present effort would develop a basis of information that would permit matching the choice of sludge treatment to the options available for disposal. Programs of investigation can be developed in relation to each of the classes of treatments for improving dewatering. Tentative programs are outlined without consideration, at this stage, of their economic merit. Rather the programs are discussed with the question in mind: what additional information would be necessary for an engineering and economic evaluation of the particular sludge treatment method?

## ADDITION OF PARTICULATE MATTER

This approach appears to be the most promising for it has been found successful in practice (<u>19</u>), and can be undertaken with greater assurance than the other treatments. In addition, it does not require any new types of equipment. If the resulting sludge is recycled some additional function of the added particulates is recovered.

To develop further the potential of this approach, answers to a number of questions need to be established. Particularly if recycling is contemplated, a more complete characterization of the effects of added particulates on drainage behavior would be necessary. A program can be designed to provide mill personnel with useful guidelines concerning the effects of specific types of particulate matter. This would utilize the approach developed by Ingmanson at the Institute (25) to characterize the drainage behavior of pulps. Ingmanson's approach would be preferred for the purpose here considered because it accounts much more adequately than Thode's method for the coupling of hydrodynamic effects and the constitutional characteristics of the fibers and added particulates.

In connection with such a program, a thorough evaluation of the potential of polymeric drainage and retention aids would also be undertaken. It is possible that under some conditions a combination of polymeric and particulate additives would be more effective than either used separately.

Another question related to particulate addition concerns the surface properties of the added particles. It is clear from the studies described in previous sections that the presence of certain functional groups at the surface of the added particles can be important to their success in aiding the drainage of the sludge. The program contemplated in this area would also focus on the nature of the groups necessary and develop some quantitative measures of the amounts which must be present for effective action. In addition, it would seek to establish whether similar functional groups attached to less expensive substrates would act equally as effectively. In connection with this approach, consideration might be given to the possibility of attaching suitable functional groups to waste fiber which could then be used as an additive dewatering aid.

PHYSICAL TREATMENTS

Freezing and heat treatment appear less promising than particulate addition because they require large amounts of energy that would be lost in the disposal process. The energy requirements are determined not by the organic solids content but rather by the large amount of water that would have to be taken through the thermal cycle. It is well known that both the heat capacity and heats of transition of water are unusually high for a liquid. In addition, the second law of thermodynamics would limit the degree to which energy can be recycled in any physical treatment method for the sludge.

In spite of all the negative factors, however, data currently available on rates and energy requirements do not provide an adequate basis for an economic evaluation. Thus, a program to provide the necessary information could be undertaken.

The program would include measurements of rates of conversion of the fibers from the hydrated to the dehydrated state. Variations of the rates with temperatures would provide indications of the energetics of the process. Observations of structural changes with the SEM and with techniques sensitive to change at the molecular level would also be undertaken to provide supporting information for interpretation of the measurements of rates and energetics.

CHEMICAL EXTRACTION AND ENZYME TREATMENT

Although these approaches have not been explored in application to sludges the effects in the drainage time studies on the holocellulose suggest the possibility of developing effective treatments. Here, however, the need for further preliminary exploration is even more acute than in the case of physical treatments.

An obvious question is suitable disposal of the extract stream. Another is provision of vessels with adequate holdup to accomplish the extraction. Finally, the cost of the reagents to be used and the degree to which they can be recovered must be considered.

Clearly a program based on chemical or enzymatic treatment of the sludges could proceed in a number of different directions. Consideration of these should be coupled with development of the economic limitations, however.

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APPENDIX I

TABLE X

ANALYSES OF EXTRACTED HOLOCELLULOSE

| | Araban, % | Xylan, % | Mannan, % | Galactan, % | Glucan, % | Galacturonic Anhydride, % | Galactan / Mannan |
|---|---|---|---|---|---|---|---|
| Holocellulose | 0.3 | 8.4 | 15.2 | 3.0 | 58.6 | 1.37 | 0.20 |
| Extracted with: | | | | | | | |
| Water at room temp., 48 hr. | 0.3 | 7.0 | 14.3 | 2.0 | 61.8 | 0.69 | 0.14 |
| Water, near boil, 3 hr. | 0.3 | 6.9 | 14.2 | 1.6 | 65.9 | 0.54 | 0.11 |
| 0.1% NaOH soln., 2 hr. | 0.2 | 6.0 | 14.9 | 1.3 | 65.9 | 0.64 | 0.087 |
| 1.0% NaOH soln., 2 hr. | 0.2 | 5.2 | 15.4 | 1.1 | 71.3 | 0.61 | 0.071 |
| 2.0% NaOH soln., 4 hr. | 0.1 | 4.0 | 14.9 | 1.2 | 73.3 | 0.78 | 0.08 |
| 4.0% NaOH soln., 20 hr. | 0.1 | 2.5 | 14.1 | 0.9 | 76.9 | 0.54 | 0.064 |
| Pectinase treatment after room temp. extraction | 0.2 | 4.8 | 14.6 | 1.5 | 66 | 0.68 | 0.10 |

Sugars — Moisture-free basis.
Methods: Sugars, Tappi 53:257(1970).
Galact. anhydride, Anal. Chem. 24:1986(1952), with chromatographic separation of galacturonic acid.

Appendix I (Continued)

TABLE XI

ANALYSES OF LIQUID EXTRACTS

| | Sugars Based on Initial Holocellulose, % | | | | | |
|---|---|---|---|---|---|---|
| | Araban | Xylan | Mannan | Galactan | Glucan | Galacturonic Anhydride |
| Prewash (to remove ethanol) | 0.06 | 1.69 | 1.38 | 0.70 | 0.47 | 0.21 |
| Water, room temp. | 0.01 | 0.32 | 0.39 | 0.15 | 0.18 | 0.09 |
| Water, near boil | 0.05 | 0.31 | 0.94 | 0.41 | 0.33 | 0.24 |
| 0.1% NaOH soln. | 0.07 | 0.89 | 0.28 | 0.46 | 0.08 | 0.20 |
| 1.0% NaOH soln. | 0.04 | 0.78 | 0.11 | 0.08 | 0.05 | 0.23 |
| 2.0% NaOH soln. | Sugar analysis invalid due to interference | | | | | 0.04 |
| 4.0% NaOH soln. | Sugar analysis invalid due to interference | | | | | 0.14 |
| Pectinase treatment extract | 0.44 | 2.17 | 1.62 | 1.76 | 0.78 | 2.39 |

Methods as in solids analysis.

APPENDIX II

PREPARATION OF GROUNDWOOD SP HOLOCELLULOSE

In preparing the holocellulose from the southern pine groundwood it was desired that the lignin be removed without affecting the content of hemicelluloses. The pulp was exhaustively chlorinated in the cold in carbon tetrachloride and the chlorolignins were removed by extraction with an alcoholic ethanolamine solution. The procedure was adapted from one developed by Thomas (13) and subsequently improved by Bernardin (15).

The southern pine groundwood, which had been broken up with a pulp breaker and stored moist at 40°F., was preextracted by suspending in 95% ethanol at room temperature for 16 hours.

Six chlorinations in sequence were applied to a 100 g., dry basis, portion of the pulp. The reaction and filtering operations were conducted in an 18-cm. coarse fritted glass funnel fitted with suitable stopper and cover. The funnel was surrounded by a cooling bath.

For each step, the pulp with excess liquid removed, was moistened with 50% aqueous ethanol at 0°C. The mix was slurried with 500 ml. carbon tetrachloride at -5°C., then with further addition of 500 ml. of a solution of chlorine in carbon tetrachloride at -10 to -5°C. (The chlorine solution was prepared by bubbling chlorine gas into the carbon tetrachloride at -10 to -5°C.) The mixture was stirred and the temperature maintained as nearly as possible in the 0 to 5°C. range. At the end of 10 minutes chlorination, excess liquid was removed and the pulp washed 4 times with a 3% solution of ethanolamine in ethanol and twice with 95% ethanol.

The pulp chlorination was exothermic, so much so in the first chlorination that a maximum temperature of 15°C. was reached in spite of stirring and the addition of 250 ml. more of carbon tetrachloride at -5°C. Subsequent chlorinations were controlled in the 0 to 5°C. range.

At the end of the sixth chlorination there was no appreciable color in the ethanolamine extract and no further change in the color of the pulp.

Holocellulose yield was 73.5% and its Klason lignin content 1%. The holocellulose, wet with 95% ethanol, was stored in a refrigerator.